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A TEXT-BOOK OF INORGANIC CHEMISTRY.

EDITED BY

J NEWTON FRIEND, D Sc, Ph D, F I C,
CARNEGIE GOLD MEDALLIST

VOLUME II.

THE ALKALI-METALS AND THEIR CONGENERS.

BY

A JAMIESON WALKER,
Ph D (H F D), B A (Q U B) F I C

With Frontispiece and Illustrations

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GENERAL INTRODUCTION TO THE SERIES

DURING the past few years the civilized world has begun to realize the advantages accruing to scientific research, with the result that an ever-increasing amount of time and thought is being devoted to various branches of science

No study has progressed more rapidly than chemistry. This science may be divided roughly into several branches namely, Organic, Physical, Inorganic, and Analytical Chemistry. It is impossible to write any single text-book which shall contain within its two covers a thorough treatment of any one of these branches, owing to the vast amount of information that has been accumulated. The need is rather for a series of text-books dealing more or less comprehensively with each branch of chemistry. This has already been attempted by enterprising firms, so far as physical and analytical chemistry are concerned, and the present series is designed to meet the needs of inorganic chemists. One great advantage of this procedure lies in the fact that our knowledge of the different sections of science does not progress at the same rate. Consequently, as soon as any particular part advances out of proportion to others, the volume dealing with that section may be easily revised or rewritten as occasion requires.

Some method of classifying the elements for treatment in this way is clearly essential, and we have adopted the Periodic Classification with slight alterations, devoting a whole volume to the consideration of the elements in each vertical column, as will be evident from a glance at the scheme in the Frontispiece.

In the first volume, in addition to a detailed account of the elements of Group 0, the general principles of inorganic chemistry are discussed. Particular pains have been taken in the selection of material for this volume, and an attempt has been made to present to the reader a clear account of the principles upon which our knowledge of modern inorganic chemistry is based.

At the outset it may be well to explain that it was not intended to write a complete text book of physical chemistry. Numerous excellent works have already been devoted to this subject, and a volume on such lines would scarcely serve as a suitable introduction to this series. Whilst Physical Chemistry deals with the general principles applied to all branches of theoretical chemistry, our aim has been to emphasize their application to inorganic chemistry, with which branch of the subject this series of text books is exclusively concerned. To this end practically all the illustrations to the laws and principles discussed in Volume I deal with inorganic substances.

Again, there are many subjects, such as the methods employed in the accurate determination of atomic weights, which are not generally regarded as forming part of physical chemistry. Yet these are sub-

suffer by delay In the spring of 1807, he was induced to offer the exposition of the principles herein contained in a course of Lectures, which were twice read in Edinburgh, and once in Glasgow. On these occasions he was honoured with the attention of gentlemen, universally acknowledged to be of the first respectability for their scientific attainments, most of whom were pleased to express their desire to see the publication of the doctrine in the present form, as soon as convenient. Upon the author's return to Manchester he began to prepare for the press Several experiments required to be repeated, other new ones were to be made, almost the whole system both in matter and manner was to be new, and consequently required more time for the composition and arrangement These considerations, together with the daily avocations of profession, have delayed the work nearly a year, and, judging from the past, it may require another year before it can be completed In the mean time, as the doctrine of heat, and the general principles of Chemical Synthesis, are in a good degree independent of the future details, there can no great detriment arise to the author, or inconvenience to his readers, in submitting what is already prepared, to the inspection of the public

GENERAL INTRODUCTION TO THE SERIES.

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as this would render them unnecessarily bulky and expensive, rather has it been to contribute concise and suggestive accounts of the various topics, and to append numerous references to the leading works and memoirs dealing with the same Every effort has been made to render these references accurate and reliable, and it is hoped that they will prove a useful feature of the series The more important abbreviations, which are substantially the same as those adopted by the Chemical Society, are detailed in the subjoined list

The addition of the *Table of Dates of Issue of Journals* (pp xix-xxvi) will, it is hoped, enhance the value of this series It is believed that the list is perfectly correct, as all the figures have been checked against the volumes on the shelves of the library of the Chemical Society by Mr F W Clifford and his staff To these gentlemen, the editor and the author desire to express their deep indebtedness

In order that the series shall attain the maximum utility, it is necessary to arrange for a certain amount of uniformity throughout, and this involves the suppression of the personality of the individual author to a corresponding extent for the sake of the common welfare It is at once my duty and my pleasure to express my sincere appreciation of the kind and ready manner in which the authors have accommodated themselves to this task, which, without their hearty co-operation, could never have been successful Finally, I wish to acknowledge the unfailing courtesy of the publishers, Messrs Charles Griffin and Co, who have done everything in their power to render the work straightforward and easy

J NEWTON FRIEND

February, 1924

PREFACE

THIS volume is concerned with the first group of the Periodic System, and gives an account of the elements hydrogen, lithium, sodium, potassium, rubidium, caesium, copper, silver, gold, and their compounds. It deals also with the radical ammonium and its principal derivatives. The reasons for the inclusion of hydrogen among the elements of Group I are considered in the Introduction. So far as the limitations of space have permitted, an attempt has been made to summarize the main work done in this field of inorganic chemistry, and by means of numerous references it is hoped to give the reader easy access to the literature of those subjects of interest to him. Many of the original papers mentioned have been consulted. In addition, valuable information has been afforded by Abegg and Auerbach's *Handbuch der anorganischen Chemie*, by Thorpe's *Dictionary of Applied Chemistry*, by the *Abstracts* and *Annual Reports* of the Chemical Society, and by the *Chemisches Zentralblatt*.

The author desires to express his hearty thanks to Dr F Challenger, F I C, for reading the proofs twice, and for making many valuable criticisms and suggestions, to Mr F W Clifford and his staff at the library of the Chemical Society for their kindness in checking the accuracy of many of the references, to Dr J Newton Friend, F I C, for numerous helpful suggestions respecting the text, and for preparing the section on the atomic weight of lithium, and also the subject index and the table of contents, to Mr H F V Little, B Sc, D I C, for writing the sections on the other atomic weights, and for making the drawing of Morley's apparatus, to Dr O E Mott, O B E, F I C, for drawing the solubility-curves, to Dr A E H Tutton, F R S, for contributing the section on the isomorphism of the sulphates and selenates of the alkali metals, and to the publishers for the care bestowed by them on the production of the volume.

Although every effort to eliminate error from the text and from the references has been made, mistakes are inevitable, and the author would be glad if readers would notify to the publishers such errors as they may observe.

A J W

February, 1924

quantities of heat in bodies of equal weight or bulk, or even the *relative quantities*, accurately ascertained, for any temperature, the numbers expressing those quantities would constitute a table of *specific heats*, analogous to a table of *specific gravities*, and would be an important acquisition to science Attempts of this kind have been made with very considerable success

Whether the specific heats, could they be thus obtained for one temperature, would express the relation at every other temperature, whilst the bodies retained their form, is an enquiry of some moment From the experiments hitherto made there seems little doubt of its being nearly so , but it is perhaps more correct to deduce the specific heat of bodies from equal *bulks* than from equal *weights* It is very certain that the two methods will not give precisely the same results, because the expansions of different bodies by equal increments of temperature are not the same But before this subject can well be considered, we should first settle what is intended to be meant by the word temperature

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Detection and Estimation	

rature, and then be raised to any other temperature, the additional quantities of heat received by each will be exactly proportioned to the whole quantities of that fluid previously contained in them This conclusion, though it may be nearly consistent with facts in general, is certainly not strictly true For, in elastic fluids, it is well known, an increase of *bulk* occasions an increase of specific heat, though the weight and temperature continue the same It is probable then that solids and liquids too, as they increase in bulk by heat, increase in their capacity or capability of receiving more This circumstance, however, might not affect the conclusion above, provided all bodies increased in one and the same proportion by heat, but as this is not the case, the objection to the conclusion appears of validity Suppose it were allowed that a thermometer ought to indicate the accession of *equal* increments of the fluid denominated caloric, to the body of which it was to shew the temperature,—suppose too that a measure of air or elastic fluid was to be the body, query, whether ought the air to be suffered to expand by the temperature, or to be confined to the same space of one measure? It appears to me the most likely in theory to procure a standard capacity for heat by subjecting a body to heat,

LIST OF CHIEF ABBREVIATIONS EMPLOYED IN THE REFERENCES

ABBREVIATED TITLE

Afhandl Fys Kem
Amer Chem J
Amer J Sci
Anal Fis Quim
Analyst
Annalen
Ann Chim
Ann Chim anal

Ann Chim Phys
Ann Mines
Ann Pharm
Ann Phys Chem
Ann Physik
Ann Physik Beibl
Ann Sci Univ Jassy
*Arbeiten Kaiserl Gesundheits
amte*
Arch exp Pathol Pharmak
Arch Pharm
Arch Sci phys nat
Atti Acc Torino
Atti R Accad Lincei
B A Reports
Ber
Ber Deut physikal Ges
Bot Zeit
Bull Acad Sci Cracow

Bull Acad roy Belg

Bull de Belg
Bull Soc chim
Bull Soc fran^c Min
Bull Soc min de France
Bull U S Geol Survey
Centr Min
Chem Ind
Chem News
Chem Weekblad
Chem Zentr
Chem Zeit
Compt rend

Crelle's Annalen

Dingl poly J
Drude's Annalen
Electrochem. Met Ind

JOURNAL

Afhandlingat i Fysik, Kem och Mineralogi
American Chemical Journal
American Journal of Science
Anales de la Sociedad Espaⁿola Fisica y Quimica
The Analyst
Justus Liebig's Annalen der Chemie
Annales de Chimie (1719–1815, and 1914 +)
*Annales de Chimie analytique appliquee a l'Industrie, a
l'Agriculture, a la Pharmacie, et a la Biologie*
Annales de Chimie et de Physique (Paris) (1816–1913)
Annales des Mines
Annalen der Pharmacie (1832–1839)
Annalen der Physik und Chemie (1819–1899)
Annalen der Physik (1799–1818, and 1900 +)
Annalen der Physik Beiblatter
Annales scientifiques de l'Universit^et de Jassy

Arbeiten aus dem Kaiserlichen Gesundheitsamte
Archiv fur experimentelle Pathologie und Pharmakologie
Archiv der Pharmazie
Archives des Sciences physique et naturelles, Geneve
Atti dell' Reale Accademia delle Scienze di Torino
Atti della Reale Accademia Lincei
British Association Reports
Berichte der Deutschen chemischen Gesellschaft
Berichte der Deutschen physikalischen Gesellschaft
Botanische Zeitung
*Bulletin international de l'Academie des Sciences de
Cracovia*
*Académie royale de Belgique—Bulletin de la Classe des
Sciences*
Bulletin de la Société chimique Belgique
Bulletin de la Société chimique de France
Bulletin de la Société fran^caise de Mineralogie
Bulletin de la Société mineralogique de l'In^{ce}nce
Bulletins of the United States Geological Survey
Centralblatt fur Mineralogie
Die Chemische Industrie
Chemical News
Chemisch Weekblad
Chemisches Zentralblatt
Chemiker Zeitung (C^othen)
*Comptes rendus hebdomadaires des Seances de l'Academie
des Sciences (Paris)*
*Chemische Annalen fur die Freunde der Naturk^{hre}, von
L. Crelle*
Dingler's polytechnisches Journal
Annalen der Physik (1900–1906)
Electrochemical and Metallurgical Industry

of bodies for heat, that the effects are such, as only to raise or depress the temperature a few degrees, when perhaps the whole mass of heat is equivalent to two or three thousand such degrees, and that a volume of air supposed to contain 2005° of temperature being rarefied till it become 2000° , or lost 5° of temperature, may still be considered as having its capacity invariable This may be granted if the data are admissible, but the true changes of temperature consequent to the condensation and rarefaction of air have never been determined I have shewn, (Manchester Mem. Vol 5, Pt 2) that in the process of admitting air into a vacuum, and of liberating condensed air, the inclosed thermometer is affected as if in a medium of 50° higher or lower temperature, but the effects of instantaneously doubling the density of air, or replenishing a vacuum, cannot easily be derived from those or any other facts I am acquainted with, they may perhaps raise the temperature one hundred degrees or more The great heat produced in charging an air-gun is a proof of a great change of capacity in the inclosed air — Upon the whole then it may be concluded, that the change of bulk in the same body by change of temperature, is productive of considerable effect on its capacity for heat, but

LIST OF CHIEF ABBREVIATIONS EMPLOYED IN THE REFERENCES

ABBREVIATED TITLE

ABBREVIATED TITLE	JOURNAL
Afhandl Fys Kem	Afhandlingat i Fysik, Kemio och Mineraloggi
Amer Chem J	American Chemical Journal
Amer J Sci	American Journal of Science
Anal Fis Quim	Anales de la Sociedad Espanola Fisica y Quimica
Analyst	The Analyst
Annalen	Justus Liebig's Annalen der Chemie
Ann Chim	Annales de Chimie (1719-1815, and 1914 +)
Ann Chim anal	Annales de Chimie analytique appliquee a l'Industrie, a l'Agriculture a la Pharmacie, et a la Biologie
Ann Chim Phys	Annales de Chimie et de Physique (Paris) (1816-1913)
Ann Mines	Annales des Mines
Ann Pharm	Annalen der Pharmacie (1832-1839)
Ann Phys Chem	Annalen der Physik und Chemie (1819-1899)
Ann Physik	Annalen der Physik (1799-1818, and 1900 +)
Ann Physik Beibl	Annalen der Physik Beiblatter
Ann Sci Univ Jassy	Annales scientifiques de l'Université de Jassy
Arbeiten Kaiserl Gesundheits amte	Arbeiten aus dem Kaiserlichen Gesundheitsamte
Arch exp Pathol Pharmak	Archiv fur experimentelle Pathologie und Pharmakologie
Arch Pharm	Archiv der Pharmazie
Arch Sci phys nat	Archives des Sciences physique et naturelles Geneve
Atti Acc Torino	Atti della Reale Accademia delle Scienze di Torino
Atti R Accad Lincei	Atti della Reale Accademia Lincei
B A Reports	British Association Reports
Ber	Berichte der Deutschen chemischen Gesellschaft
Ber Deut physikal Ges	Berichte der Deutschen physikalischen Gesellschaft
Bot Zeit	Botanische Zeitung
Bull Acad Sci Cracow	Bulletin international de l'Academie des Sciences de Cracovie
Bull Acad roy Belg	Academie royale de Belgique—Bulletin de la Classe des Sciences
Bull de Belg	Bulletin de la Societe chimique Belge
Bull Soc chim	Bulletin de la Société chimique de France
Bull Soc franç Min	Bulletin de la Société française de Mineralogie
Bull Soc min de France	Bulletin de la Société mineralogique de France
Bull U S Geol Survey	Bulletins of the United States Geological Survey
Centr Min	Centralblatt fur Mineralogie
Chem Ind	Die Chemische Industrie
Chem News	Chemical News
Chem Weekblad	Cnemisch Weekblad
Chem Zentr	Chemisches Centralblatt
Chem Zeit	Chemiker Zeitung (Cothen)
Compt rend	Comptes rendus hebdomadaires des Seances de l'Academie des Sciences (Paris)
Crell's Annalen	Chemische Annalen fur die Freunde der Naturlehre von L Crell
Dingl poly J	Dingler's polytechnisches Journal
Drude's Annalen	Annalen der Physik (1900-1906)
Electrochem. Met Ind	Electrochemical and Metallurgical Industry

two liquids will agree in giving the same mean temperature upon being mixed as above.

In the present imperfect mode of estimating temperature, the equable expansion of mercury is adopted as a scale for its measure. This cannot be correct for two reasons, 1st the mixture of water of different temperatures is always *below* the mean by the mercurial thermometer, for instance, water of 32° and 212° being mixed, gives 119° by the thermometer, whereas it appears from the preceding remarks, that the temperature of such mixture ought to be found above the mean 122°, 2d mercury appears by the most recent experiments to expand by the same law as water, namely, as the square of the temperature from the point of greatest density — The apparently equal expansion of mercury arises from our taking a small portion of the scale of expansion, and that at some distance from the freezing point of the liquid

From what has been remarked it appears that we have not yet any mode easily practicable for ascertaining what is the true mean between any two temperatures, as those of freezing and boiling water, nor any thermometer which can be considered as approximating nearly to accuracy

Heat is a very important agent in nature, it

LIST OF CHIEF ABBREVIATIONS

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ABBREVIATED TITLE	JOURNAL
Sitzungsber K Akad Wiss Wien	Sitzungsberichte der Königlich bayerischen Akademie der Wissenschaften zu Wien.
Sci Proc Roy Dubl Soc.	Scientific Proceedings of the Royal Dublin Society
Techn Jahresber	Jahresbericht über die Leistungen der Chemischen Technologie
Trans Amer Electrochem Soc	Transactions of the American Electrochemical Society
Trans Chem Soc	Transactions of the Chemical Society
Trans Inst Min Eng	Transactions of the Institution of Mining Engineers
Trav et Mem du Bureau intern des Poids et Mesures	Travaux et Mémoires du Bureau International des Poids et Mesures
Verh Ges deut Naturforsch Aerzte	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte
Wied Annalen	Wiedermann's Annalen der Physik und Chemie (1877-1899)
Wissenschaftl Abhandl phys tech Reichsanst	Wissenschaftliche Abhandlungen der physikalisch technischen Reichsanstalt
Zeitsch anal Chem	Zeitschrift für analytische Chemie
Zeitsch angew Chem	Zeitschrift für angewandte Chemie
Zeitsch anorg Chem	Zeitschrift für anorganische Chemie
Zeitsch Chem	Kritische Zeitschrift für Chemie
Zeitsch Chem Ind Kolloide	Zeitschrift für Chemie und Industrie des Kolloide (continued as Kolloid Zeitschrift)
Zeitsch Elektrochem	Zeitschrift für Elektrochemie
Zeitsch Kryst Min	Zeitschrift für Krystallographie und Mineralogie
Zeitsch Nahr Genuss m	Zeitschrift für Untersuchung der Nahrungs und Genussmittel
Zeitsch physikal Chem	Zeitschrift für physikalische Chemie, Stochiometrie und Verwandtschaftslehre
Zeitsch physiol Chem	Hoppe Seyler's Zeitschrift für physiologische Chemie
Zeitsch wiss Photochem	Zeitschrift für wissenschaftliche Photographie, Photophysik, und Photochemie

is as the square of the temperature from their respective freezing points. Water very nearly accords with this law according to the present scale of temperature, and the little deviation observable is exactly of the sort that ought to exist, from the known error of the equal division of the mercurial scale. By prosecuting this enquiry I found that the mercurial and water scales divided according to the principle just mentioned, would perfectly accord, as far as they were comparable, and that the law will probably extend to all other pure liquids, but not to heterogeneous compounds, as liquid solutions of salts.

If the law of the expansion of liquids be such as just mentioned, it is natural to expect that other phenomena of heat will be characteristic of the same law. It may be seen in my Essay on the Force of Steam (Man Mem Vol 5, Part 2) that the elastic force or tension of steam in contact with water, increases *nearly* in a geometrical progression to equal increments of temperature, *as measured by the common mercurial scale*, it was not a little surprising to me at the time to find such an approach to a regular progression, and I was then inclined to think, that the want of perfect coincidence was owing to inaccuracy in the division of the received thermometer, but

TABLE OF DATES OF ISSUE OF JOURNALS.

FOR the sake of easy reference, a list is appended of the more important journals in chronological order, giving the dates of issue of their corresponding series and volumes. In certain cases the volumes have appeared with considerable irregularity, in others it has occasionally happened that volumes begun in one calendar year have extended into the next year, even when this has not been the general habit of the series. To complicate matters still further, the title-pages in some of these latter volumes bear the later date—a most illogical procedure. In such cases the volume number appears in the accompanying columns opposite both years. In a short summary of this kind it is impossible to give full details in each case, but the foregoing remarks will serve to explain several apparent anomalies.

Year	Amer J Sci	Ann Chum Phys	Ann Min	Arch Pharm	Dingl Poly J	Gilbert's Annalen	J Pharm Chum	Phil Mag	Phil Trans	Pogg Annalen
1800		(1) 32-35				4-6		5-8	90	
1		36-39				7-9		8-11	91	
2		40-43				10-12		11-14	92	
3		44-47				13-15		14-17	93	
4		48-51				16-18		17-20	94	
1805		52-55				19-21		20-28	95	
6		56-60				22-24		28-26	96	
7		61-64				27		26-29	97	
8		65-68				28-30		29-32	98	
9		69-72				31-33	(1) 1*	33-34	99	
1810		73-76				34-36	2	35, 36	100	
11		77-80				37-39	3	37, 38	101	
12		81-84				40-42	4	39, 40	102	
13		85-88				43-45	5	41, 42	103	
14		89-92				46-48	6	43, 44	104	
1815		93-96				49, 51	(2) 1	45, 46	105	
16		(2) 1-8				52, 54	2	47, 48	106	
17		4 6	1, 2			55, 57	3	49, 50	107	
18		7-9	3			58, 60	4	51, 52	108	
19	(1) 1	10-12	4			61, 63	5	53, 54	109	
1820	2	13-15	5		1-3	64, 66	6	55, 56	110	
21	3	16-18	6		4-6	67, 69	7	57, 58	111	
22	4, 5	19-21	7	1, 2	7-9	70, 72	8	59, 60	112	
23	6	22-24	8	3 6	10, 12	73-75	9	61, 62	113	
24	7, 8	25-27	9	7-10	13, 1	76	10	63, 64	114	1 2
1825	9	28-30	10, 11	11-14	16, 18		11	65, 66	115	3-5
26	10, 11	31-33	12, 13	15-19	19, 22		12	67, 68	116	6-8
27	12	34-36	(2) 1, 2	20-23	23, 26	Continued as Pogg Annalen	13	(2) 1, 2	117	9-11
28	13, 14	37-39	3, 4	24-26	27-30		14	3, 4	118	12-14
29	15, 16	40-42	5, 6	27-30	31-34		15	5, 6	119	15-17

* First series known as *Bulletin de l'Institut*.

expansion as the permanently elastic fluids I had formerly conjectured that air expand as the *cube* of the temperature from absolute privation, as hinted in the essay above-mentioned, but I am now obliged to abandon that conjecture

The union of so many analogies in favour the preceding hypothesis of temperature is almost sufficient to establish it, but one remarkable trait of temperature derived from experiments on the heating and cooling of bodies which does not accord with the received scale and which, nevertheless, claims special consideration, is, that *a body in cooling loses heat in proportion to its excess of temperature above that of the cooling medium*, or that the temperature descends in geometrical progression in equal moments of time Thus if a body were 1000° above the medium, the times in cooling from 1000° to 100, from 100 to 10, and from 10 to 1°, ought all to be the same This, though nearly, is not accurately true, if we adopt the common scale, as is well known, the times in the lower intervals of temperature are found longer than in the upper, but the new scale proposed, by shortening the lower degrees, and lengthening the higher, is found perfectly according to this remarkable law of heat

TABLE OF DATES OF ISSUE OF JOURNALS

Year	Amey Chem	Amey J Sci	Analyst	Annalen Suppl	Annalen Phys	Ann Mines	Aich Pharm	Ber	Bull Soc chim	Chem. News	Chem Trade J	Chem Zeit	
1860		29 30		118-119 ^b	58-60 61-60	17, 18 19, 20	101-104 105-108 (6) 1, 2		2	1, 3, 4			
61	31	32		117-120	1	19, 20	109-112		3	3, 6			
62	33	34		121-124	64-66	3, 4	113-116		4	6, 6			
63	35	36		125-128	67-69	5, 6	117-120		5	7, 8			
64	37	38		129-132	(4) 1-3				(2) 1, 2	9, 10			
1861	39	40		133-136	3 4	4-6	7, 8	121-124	3, 4	11, 12			
66	41	42		137-140	4	7-9	9, 10	125-128	5, 6	13, 14			
67	43	44		141-144	1	10-12	11, 12	129-132	7, 8	15, 16			
68	44	45		145-148	6	13-15	13, 14	133-136	9, 10	17, 18			
69	47	48		149-152		16-18	15, 16	137-140	2	11, 12	19, 20		
1870	49, 0			153-156	7	19-21	17, 18	141-144	3	13, 14	21, 22		
71	(3) 1, 2			157-160	22-24	19, 20	145-148	4	15, 16	23, 24			
72	3 4			161-164	8	25-27	(7) 1, 2	149-150 201 *	5	17, 18	25, 26		
73	5 6			165-170	28-30	3, 4	201-203	6	19, 20	27, 28			
74	7 8			171-174	(6) 1-3	5, 6	204, 205	7	21, 22	29, 30			
1875	9 10			175-179	4-6	7, 8	206, 207	8	23, 24	31, 32			
76	11 12			180-183	7-9	9, 10	208, 209	9	25, 26	33, 34			
77	13, 14	2		184-189	10-12	11, 12	210, 211	10	27, 28	35, 36			
78	15 16	3		190-194	13-15	13, 14	212, 213	11	29, 30	37, 38			
79	1	17 18		195-199	16-18	15, 16	214, 215	12	31, 32	39, 40			
1880	1, 2	19, 20		200-203	19-21	17, 18	216, 217	13	33, 34	41, 42			
81	2, 3	21, 22		206-210	22-24	19, 20	218, 219	14	35, 36	43, 44			
82	3, 4	23, 24		211-215	25-27	(8) 1, 2	220	15	37, 38	45, 46			
83	4 5	25, 26		216-221	28-30	3 4	221	16	39, 40	47, 48			
84	5 6	27, 28		222-226	(6) 1-3	5, 6	222	17	41, 42	49, 50			
1885	6 7	29, 30		227-231	4-6	7, 8	223	18	43, 44	51, 52			
86	7 8	31, 32		232-236	7-9	9, 10	224	19	45, 46	53, 54			
87	9	33, 34		237-242	10-12	11, 12	225	20	47, 48	55, 56			
88	10	35, 36		243-249	13-15	13, 14	226	21	49, 50	57, 58			
89	11	37, 38		250-256	16-18	15, 16	227	22	(3) 1, 2	59, 60			

written as (3) 1, 2, 3, etc

* Joining series 1 and 2

NEW TABLE OF TEMPERATURE.

True equal interv- als of temp on merc scale from freezing merc.	Roots, or inter- vals of temp on merc scale from freezing merc.	Squares, or mea- sures of column, or Faren heit's scale.	Same as preceding or Faren heit's scale.	Common Farenheit's scale; or preceding column cor- rected for expansion of glass.	Water Expan- sion or square of temp	Air. Expan- sion of air vapour in water geom. progress Ratio 1.0379	Force of vapour of water geom. prog ratio 1.321 In. M.	Va-
—175°	0	0	—40°			692	—	
—68°	4 3808	18 88	—21 12			837	6	012
—58	4 7908	22 94	—17 06			842	5	016
—48	5 2018	27 04	—13 96			867	7	.022
—38	5 6118	31 58	—8 52			888	3	.048
—28	6 0223	36 24	—3 76			899	—	.088
—18	6 4328	41 84	1 84			915	2	.050
—8	6 8438	46 78	6 78			931	5	.066
2	7 2538	52 63	12 68		16	948	2	.087
12	7 6648	58 74	18 74		9	965	2	.116
22	8 0748	65 81	25 81		4	982	4	.151
32	8 4858	72 —	32°			1000	200	.184
42	8 8958	79 1	39 1	39 8	0	1017	9	.264
52	9 3063	86 6	46 6	47 —	1	1036	1	.348
62	9 7168	94 44	54 44	55 —	4	1054	7	.461
72	10 1273	102 55	62 55	63 3	9	1073	5	.609
82	10 5378	110 04	71 04	72 —	16	1091	7	.804
92	10 9483	119 84	79 84	81 —	25	1111	3	1.062
102	11 3588	129 02	89 02	90 4	36	1132	2	1.40
112	11 7693	138 49	98 49	100 1	49	1152	4	1.85
122	12 1798	148 3	108 3	110 —	64	1173	1	2.46
132	12 5903	158 5	118 5	120 1	81	1194	—	3.24
142	13 0008	169 —	129 —	130 4	100	1215	4	4.87
152	13 4113	179 9	139 9	141 1	121	1237	1	5.65
162	13 8218	191 —	151 —	152 —	144	1259	2	6.69
172	14 2323	202 4	162 4	163 2	169	1281	8	7.47
182	14 6428	214 4	174 4	175 —	196	1304	7	9.87
192	15 0533	226 5	186 5	186 9	225	1328	1	10.49
202	15 4638	239 —	199 —	199 2	256	1351	8	12.85
212	15 8748	252 —	212 —	212 —	289	1376	10	15.75
312	19 9793	399 1	359 1			1443	485	
412	24 0843	579 8	539 8			1912		
512	28 1893	794 7	754 7			2148		
612	32 2943	1043 —	1000			2177		
712	336 399	1325 —	1285			3339		

TABLE OF DATES OF ISSUE OF JOURNALS

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Year	Phil Trans	Pogg Annalen	Proc Chem Soc	Proc Rov Soc	Quart J Chem Soc	Sitzungsber K Akad Wiss Wien	Rec Trav Chum	Stahl und Eisen	Wied Annalen	Zeitsch anal Chem	Zeitsch angew Chem	Zeitsch Kryst Min	Zeitsch physikal Chem
1860	150	109-111 112-114	10, 11 11	10, 11 11	13 14	39-42 43, 44							
61	151	115-117		11, 12	(continued as J Chem Soc)	45, 46							
62	152			12, 13		47, 48							
63	153	118-120		13		49, 50							
64	154	121-123											
1865	155	124-126		14									
66	156	127-129		15									
67	157	130-132		15, 16									
68	158	133-135		16, 17									
69	159	136-138		17, 18									
1870	160	139-141		18, 19									
71	161	142-144		19, 20									
72	162	145-147		20, 21									
73	163	148-150		21, 22									
74	164	151-153		22, 23									
1875	165	154-156		23, 24									
76	166	157-159		24, 25									
77	167	160		25, 26									
78	168, 169	Continued as Wied Annalen		27, 28									
79	170			28, 29, 30									
1880	171			30, 31									
81	172			31, 32, 33									
82	173			33, 34									
83	174			34, 35, 36									
84	175			36, 37, 38									
1885	176			1	38, 39								
86	177			2	40, 41								
87	A 178			3	42, 43								
88	179			4	43, 44, 45								
89	180			5	45, 46, 47								

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being 12° , but below 32° and above 212° , the differences become more remarkable

The 2d and 3d columns are two series, the one of roots, and the other of their squares They are obtained thus, opposite 32° , in the first column, is placed in the 3d, 72° , being the number of degrees or equal parts in Fahrenheit's scale from freezing mercury to freezing water, and opposite 212° in the first is placed 252° in the 3d, being $212 + 40^{\circ}$, the number of degrees (or rather equal parts) between freezing mercury and boiling water The square roots of these two numbers, 72° and 252° , are found and placed opposite to them in the second column The number 8 4853 represents the relative quantity of real temperature between freezing mercury and freezing water, and the number 15 8743 represents the like between freezing mercury and boiling water, consequently the difference 7 3890 represents the relative quantity between freezing water and boiling water, and $7 \frac{3}{8}90 - 18 = 410$ represents the quantity corresponding to each interval of 10 By adding 410 successively to 8 4853, or subtracting it from it, the rest of the numbers in the column are obtained, which are of course in arithmetic progression The numbers in the 3d column are all obtained by squaring those of

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Year	Dingl Poly J	Gazzetta	J Amer Chem Soc	J Ind King Chem	J Pharm Chem	J Physical Chem	J prakt Chem	J Russ Phys Chem Soc	J Soc Chem Ind	Monatsh	Nature	Phil Mag
1890	275-278 279-282	20 21	12 13	57, 58 39, 60	21, 22 23, 24	41, 42 45, 44	22 23	9 10	11 12	35, 36 37, 38	41, 42, 43 43, 44, 45	29, 30 31, 32
91	283-286	22	14	61, 62	25, 26	45, 46	24	11	13	39, 40	45, 46, 47	33, 34
92	287-290	23	15	63, 64	27, 28	47, 48	25	12	14	41, 42	47, 48, 49	35, 36
93	291-294	24	16	65, 66	29, 30	49, 50	26	13	15	43, 44	49, 50, 51	37, 38
94	295-298 299-302	25 26	17 18	67, 68 69, 70	(6) 1, 2 3, 4	51, 52 53, 54	27	14	16	45, 46	51, 52, 53	39, 40
95	303-306	27	19	71, 72	5, 6	55, 56	28	15	17	47, 48	53, 54, 55	41, 42
96	307-310	28	20	73, 74	7, 8	57, 58	30	16	18	49, 50	55, 56, 57	43, 44
97	311-314	29	21	75, 76	9, 10	59, 60	31	17	19	51, 52	57, 58, 59	45, 46
98	315-318	30	22	77, 78	11, 12	61, 62	32	18	20	53, 54	59, 60, 61	47, 48
99	319-322	31	23	79, 80	13, 14	63, 64	33	19	21	55, 56	61, 62, 63	49, 50
1900	323-326	32	24	81, 82	15, 16	65, 66	34	20	22	57	63, 64, 65	(6) 1, 2
01	327-330	33	25	83, 84	17, 18	67, 68	35	21	23	58	65, 66, 67	3, 4
02	331-334	34	26	85, 86	19, 20	69, 70	36	22	24	59	67, 68, 69	5, 6
03	335-338	35	27	87, 88	21, 22	71, 72	37	23	25	60, 61	69, 70, 71	7, 8
04	339-342	36	28	89, 90	10, 11	73, 74	38	24	26	62, 63	71, 72, 73	9, 10
05	343-346	37	29	91, 92	12, 13	75, 76	39	25	27	64, 65	73, 74, 75	11, 12
06	347-350	38	30	93, 94	14, 15	77, 78	40	26	28	66, 67	75, 76, 77	13, 14
07	351-354	39	31	95, 96	16, 17	79, 80	41	27	29	68, 69	77, 78, 79	15, 16
08	355-358	40	32	97, 98	18	81, 82	42	28	30	70, 71	79-82	17, 18
09	359-362	41	33	99, 100	2, 3, 4	83, 84	43	31	72, 73	82-85	19, 20	
10	363-366	42	34	101, 102	5, 6	85, 86	44	32	74, 75	85-88	21, 22	
11	367-370	43	35	103, 104	7, 8	87, 88	45	33	76, 77	88, 89, 90	23, 24	
12	371-374	44	36	105, 106	9, 10	89, 90	46	34	78, 79	90, 91, 92	25, 26	
13	375-378	45	37	107, 108	11, 12	91, 92	47	35	80, 81	92, 93, 94	27, 28	
14	379-382	46	38	109, 110	13, 14	93, 94	48	36	82	94, 95, 96	29, 30	
15	383-386	47	39	111, 112	15, 16	95, 96	49	37	83	96, 97, 98	31, 32	
16	387-390	48	40	113, 114	17, 18	97, 98	50	38	84	98, 99, 100	33, 34	
17	391-394	49	41	115, 116	19, 20	99, 100	51	39	85	100-102	35, 36	
18	395-398	40	42	117, 118	21, 22	101, 102	52	40	86	102-104	37, 38	
19	399-402	41	43	119, 120	23	103, 104	53					

* See footnote, p. xx

not for this increase Not however to over-rate the effect, I have taken it only at $1^{\circ} 7$, making the number 108° , 3 in the 4th column, 110° in the 5th, and the rest of the column is corrected accordingly The numbers in this column cannot well be extended much beyond the interval from freezing to boiling water, for want of experiments on the expansion of glass By viewing this column along with the 1st, the quantity of the supposed error in the common scale may be perceived , and any observations on the old thermometer may be reduced to the new

The 6th column contains the squares of the natural series 1, 2, 3, &c representing the expansion of water by equal intervals of temperature Thus, if a portion of water at 42° expands a quantity represented by 289, at the boiling temperature, then at 52° it will be found to have expanded 1, at 62° , 4 parts, &c &c Water expands by cold or the abstraction of heat in the same way below the point of greatest density, as will be illustrated when we come to consider the absolute expansion of bodies The apparent greatest density too does not happen at $39^{\circ}, 3$ old scale , but about 42° , and the greatest real density is it or near 36° of the same

The 7th column contains a series of num-

A TEXT-BOOK OF INORGANIC CHEMISTRY.

VOL II

THE ALKALI-METALS AND THEIR CONGENERS

CHAPTER I INTRODUCTION

THE first group of the periodic system¹ includes *hydrogen* ($H=1\ 008$), the alkali-metals *lithium* ($Li=6\ 94$), *sodium* ($Na=23\ 00$) *potassium* ($K=39\ 10$), *rubidium* ($Rb=85\ 45$), and *caesium* ($Cs=132\ 81$), and the metals *copper* ($Cu=63\ 57$), *silver* ($Ag=107\ 88$), and *gold* ($Au=197\ 2$). The inclusion of hydrogen in Group I was suggested by Mendeléeff,² but the arrangement has been subjected to much adverse criticism, many chemists preferring to class it with the halogens as the first member of Group VII. An account of the arguments advanced by both schools of thought is given on pp 6 to 8. The close resemblance of the compounds formed by the interaction of ammonia³ and acids to the metallic salts, and especially to the salts of potassium, makes it desirable to include these compounds in a description of the derivatives of the elements of Group I. They contain the univalent radical *ammonium*, NH_4 (p 8).

The Alkali-Metals

The name *alkali* is derived from the Arabic *Al kalyun*, meaning the ashes of sea-plants and land plants. Prior to the French Revolution the carbonates of sodium and potassium were manufactured by lixiviation of these ashes, and, on the isolation of sodium and potassium (pp 82 and 152), the name was employed to denote the group of which they are typical.

The inclusion of iron, cobalt, nickel, and certain other metals in Group VIII⁴ enables the alkali metals lithium, sodium, potassium, rubidium, and caesium to be placed in their natural position as a sub-group of Group I of the periodic system, in juxtaposition to the related sub-group containing copper, silver, and gold (p 8). This arrangement

¹ See Frontispiece

² This series, Vol VI

³ Mendeléeff, *Annalen*, 1872, Suppl 8, 133

⁴ This series Vol IX

those numbers do not differ from the table just referred to, which was the result of actual experience, so much as 2° in any part; a difference that might even exist between two thermometers of the same kind

The 9th column exhibits the force of the vapour of sulphuric ether in contact with liquid ether, which is a geometrical progression, having a less ratio than that of water. Since writing my former Essay on the Force of Steam, I am enabled to correct one of the conclusions therein contained, the error was committed by trusting to the accuracy of the common mercurial thermometer. Experience confirmed me that the force of vapour from water of nearly 212° , varied from a change of temperature as much as vapour from ether of nearly 100° . Hence I deduced this general law, namely, "that the variation of the force of vapour from all liquids is the same for the same variation of temperature, reckoning from vapour of any given force"—But I now find that 30° of temperature in the lower part of the common scale is much more than 30 in the higher and therefore the vapours of ether and water are not subject to the same change of force by equal increments of temperature. The truth is, vapour from water, ether and other liquids, increases in force in geometri-

production of strongly basic hydroxides of the formula $M\text{OH}$, distinguished by their great solubility in water, their very caustic nature, and their complete stability at high temperatures. According to Hackspill,¹ no action on ice can be detected for sodium at -98°C , for potassium at -105°C , for rubidium at -108°C , and for caesium at -116°C . These results indicate that rise in the atomic weight of the metals is accompanied by a development in the electropositive character. They neutralize all acids, forming salts of the type $M\text{X}$ in which the metal is univalent. The chemical activity of the members of the series increases with their atomic weights in the order lithium, sodium, potassium, rubidium, and caesium.

Despite the close resemblance between the members of the alkali-group, important differences in character must be noted. The properties of certain salts of lithium and sodium present a marked contrast to those of the corresponding salts of potassium, rubidium, and caesium. While the normal carbonates and phosphates of all other metals are insoluble in water, those of the alkali-metals dissolve, but the carbonate and phosphate of lithium are characterized by their comparatively slight solubility (pp. 74 and 76). In this respect lithium displays more analogy to the alkaline-earth-metals than to its companions in Group I. A similar difference in character between the first member of a group and the succeeding members is displayed in other instances.² Potassium, rubidium, and caesium differ from lithium and sodium in forming comparatively insoluble chloroplatinates and primary tartrates, and deliquescent carbonates. Lithium and sodium, members of the two short periods, possess the general group-character, whereas potassium, rubidium, and caesium, belonging to long periods, display almost complete homology.

Copper, Silver, and Gold

The metals copper, silver, and gold occupy corresponding positions in the three long periods of the periodic system, and furnish a connecting link between the high melting and non volatile metals nickel, palladium, and platinum of Group VIII³ and the readily fused volatile metals zinc, cadmium, and mercury of Group II.⁴ Their relationship to the alkali metals, especially to sodium, is analogous to that of zinc, cadmium, and mercury to magnesium. These analogies are illustrated by the subjoined table of atomic weights.

Na = 23.00	Mg = 24.32
Ni = 58.68	Cu = 63.57
Pd = 106.7	Ag = 107.88
Pt = 195.2	Au = 197.2
	Hg = 200.6

The atomic volumes and coefficients of expansion display a similar relationship.

Some of the physical constants of the copper group are cited in the appended table.

¹ Hackspill *Ann. Chim. Phys.* 1913, [8] 28 613.

Compare carbon (this series, Vol V), glucinum (this series, Vol III) and fluorine (this series, Vol VIII).

² This series, Vol IX, Part I.

⁴ *Ibid.* Vol III.

sible to have a portion of liquid remaining in contact with the vapour

The 10th column shews the force of vapour from alcohol, or rather common spirit of wine, determined by experiment in the same way as the vapour of water. This is not a geometrical progression, probably because the liquid is not pure and homogeneous. I suspect the elastic fluid in this case is a mixture of aqueous and alcoholic vapour.

SECTION 2

EXPANSION BY HEAT

One important effect of heat is the expansion of bodies of every kind. Solids are least expanded, liquids more, and elastic fluids most of all. The quantities of increase in bulk have in many instances been determined, but partly through the want of a proper thermometer, little general information has been derived from particular experiments. The force necessary to counteract the expansion has not been ascertained, except in the case of elastic fluids, but there is no doubt it is very great. The quantity and law of expansion of all permanent elastic fluids have already

are not decomposed by heat, but cupric oxide is converted into cuprous oxide, and the elimination of the oxygen from the oxides of silver and gold can be effected without the application of excessive heat

The cupric compounds, CuX_2 , show a marked resemblance to those of the metals of Group II and to those of other metals characterized by their bivalence, an example being the similarity of constitution and isomorphism of cupric sulphate with the sulphates of magnesium and zinc, and with the *ous* sulphates of iron, nickel, cobalt, and manganese. All these sulphates combine with those of the alkali metals to form double salts analogous in constitution and crystal form. Isomorphism is also a feature of the corresponding carbonates, MCO_3 , chlorates, $\overset{II}{M}(ClO_3)_2 \cdot 6H_2O$, and bromates, $\overset{II}{M}(BrO_3)_2 \cdot 6H_2O$

The auric compounds, AuX_3 , are related to the corresponding derivatives of such tervalent metals as aluminium, $\overset{III}{AlX}_3$, and indium, InX_3 , another instance of the close connexion subsisting between the valency of a metal and the typical characteristics of the compounds derived from it. Three series of oxides are given below, the compounds formed from each member being similar in character to the corresponding compounds of the same series.

Na_2O Sodium	Ag_2O Silver	Cu_2O Cuprous	Au_2O Aurous	Tl_2O Thallous
MgO Magnesium	ZnO Zinc	CuO Cupric	FeO Ferrous	HgO Mercuric
Al_2O_3 Aluminium	Fe_2O_3 Ferric	Au_2O_3 Auric	Tl_2O_3 Thallic	

Chromium,¹ manganese,² and iron³ also exemplify the alteration in the character of compounds occasioned by a change of valency. In the first series even the heavy metals have a very positive and basic character, silver oxide and thallous oxide being strong bases, and cuprous oxide and aurous oxide having a more pronounced basic character than the corresponding higher oxides. The oxides of the third series are slightly acidic, a characteristic associated with the somewhat metalloidal character of the tervalent metals from which they are derived. The hydrogen of aluminium hydroxide, $Al(OH)_3$, and of auric hydroxide, $Au(OH)_3$, resembles that of boric acid, $B(OH)_3$, in being replaceable by alkali metals with formation of compounds of the type $Al(ONa)_3$. Indium oxide, In_2O_3 , is also soluble in alkalies, but does not appear to form a definite compound.

The alkali metals are distinguished from the heavy metals of the copper group by the formation of very stable hydroxides and carbonates. Copper hydroxide, $Cu(OH)_2$, is very easily decomposed into the oxide and water, and the hydroxides of silver and gold have not been isolated. The behaviour of the carbonates is similar, thus, silver carbonate is rapidly decomposed at $200^\circ C$, with evolution of carbon dioxide.⁴

The compounds of the alkali metals with weak anions, such as O'' or

¹ This series, Vol VII

² *Ibid*, Vol VIII

³ *Ibid*, Vol IX

⁴ Joulin, *Ann Chim Phys*, 1873, [4], 30, 260

rest; in this case if temperature be added uniformly, the liquid will appear to descend with a velocity uniformly retarded to a certain point, there to be stationary, and afterwards to ascend with an uniformly accelerated velocity of the same sort as the former — For, as the velocity with which the liquid expands is uniformly accelerative, it must successively pass through all degrees from 0 to any assigned quantity, and must therefore in some moment be the same as that of the vessel, and therefore, for that moment, the liquid must appear stationary previously to that time the liquid must have descended by the third proposition, and must afterwards ascend, by the 2d but not uniformly Let the absolute space expanded by the liquid at the moment of equal velocities be denoted by 1, then that of the vessel in the same time must be 2, because the velocity acquired by an uniformly accelerating force, is such as to move a body through twice the space in the same time It follows then that the liquid must have sunk 1, being the excess of the expansion of the vessel above that of the liquid Again, let another portion of temperature equal to the former be added, then the absolute expansion of the liquid will be 4, reckoned from the commencement, and the expansion of the vessel

strong reason for not placing it in Group VII, since it indicates that the first member of the halogen group must be more electronegative than fluorine, the most electronegative of all the elements. So convinced was Mendeleeff as to the antithesis between hydrogen and the halogens, that in his last speculations¹ as to the possibility of the existence of still undiscovered elements he discusses a hypothetical member of the seventh group with an atomic weight of about 3.

In 1872 Newlands² associated hydrogen with chlorine, because chlorine can replace hydrogen in organic compounds without material alteration in the character of the substances, and because he considered that its atomic weight shows it to be the lowest member of the halogen group.

Masson³ has given a number of reasons for including hydrogen in Group VII. A summary of his views is appended.

1 Hydrogen is univalent.⁴

2 The molecule of hydrogen, like that of a halogen, is diatomic, but the molecule of an alkali-metal is monatomic.

3 The gaseous character and very low boiling-point of hydrogen. The alkali-metals are solid at ordinary temperatures, and increasing atomic weight is accompanied by a fall in boiling-point.

4 The average difference between the atomic weights of the adjacent members of a horizontal series is 3, so that by placing hydrogen at the head of Group VII it is brought next to helium with the atomic weight 4, the first member of the zero group.⁵ Since the mean difference between the atomic weights of successive members of the same group is 16, this arrangement brings hydrogen into line with fluorine, the difference of their atomic weights being 18, and that of hydrogen and lithium 6.

5 Both the liquid and solid forms of hydrogen lack metallic properties,⁶ thus, the liquid is a non conductor of electricity.

6 The mutual replaceability of hydrogen and chlorine in organic compounds, first noticed by Dumas. It should be observed that in substitution in inorganic compounds hydrogen displays a much closer analogy to the alkali metals than to the halogens, as is illustrated by the acids and the corresponding salts (p. 6).

Moissan⁷ found that the hydrides of lithium, sodium, potassium, rubidium, and cesium are non conductors of electricity, and therefore cannot be regarded as alloys. He considered that in these compounds hydrogen has a metalloidal character, and that it is not comparable with the metals, an argument against its inclusion in Group I.⁸

Both the electrochemical character of the element (p. 6) and its behaviour as in inorganic substituent (*ut supra*) seem to indicate the desirability of including it in Group I, the arrangement adopted in

¹ Mendeleff *Prometheus* 1903 15 145-151. *Chem. Cent.* 1904 1 138
Newlands *Chem. News* 1896 72 305

² Masson *ibid.* 283

³ The univalency of hydrogen cannot be regarded as an argument for preferring Group VII to Group I. A more cogent reason is the non valant character of its valency, in which it is akin to the alkali metals.

⁴ This series Vol. 1

⁵ It should be noted that hydrogen resembles the metals in crystallizing in the cubic system (p. 20). It also has the power of displacing certain metals from solutions of their salts (p. 26).

⁶ Moissan, *Compt. rend.*, 1903, 136 591

⁷ Compare Brauner *Chem. News*, 1901, 84, 233, and lithium hydride (p. 59).

by another portion it will be 5, by another &c., as before

The truth of the above proposition may be otherwise shewn thus

Let 1, 4, 9, 16, 25, &c., represent the absolute expansions of the liquid, and p , $2p$, $3p$, $4p$, $5p$, &c., those of the vessel by equal increments of temperature, then $1-4=2p$, $9-3p$, $16-4p$, $25-5p$, &c., will represent the apparent expansion of the liquid, the differences of these last quantities namely $3-p$, $5-p$, $7-p$, $9-p$, &c., form a series in arithmetical progression, the common difference of which is 2. But it is demonstrated by algebraists, that the difference of a series of square numbers, whose roots are in arithmetical progression, form an arithmetical progression, and that the common difference of the terms of this progression is equal to twice the square of the difference of the roots. Hence, as $2 = \text{twice the square of } 1$ we have the above arithmetical series $3-p$, $5-p$, &c., equal to the differences of a series of squares, the common difference of the roots of which is 1.

Now to apply these principles solid bodies are generally allowed to expand uniformly within the common range of temperature at all events the quantity is so small compared

solution of sodium or potassium hydroxide, 5 per cent of ionized ammonium hydroxide molecules being present in a tenth-normal solution, as against 91 per cent of ionized potassium hydroxide molecules in a solution of similar concentration. The quaternary ammonium bases or tetra alkylammonium hydroxides are organic derivatives of ammonium hydroxide formed by replacement of the four hydrogen atoms of the ammonium radical by alkyl-groups. An example of these compounds is tetramethylammonium hydroxide, $N(CH_3)_4OH$. Their degree of ionization in aqueous solution is proved by the electric conductivity, which is comparable with that of the hydroxides of sodium and potassium. They are thick liquids of strongly alkaline reaction, and in chemical character closely resemble these bases. It is reasonable to assume that if ammonium hydroxide could attain the same concentration in solution as a quaternary ammonium base, it would exhibit similar electric conductivity. The dissimilarity of ammonium hydroxide in this respect is due to its decomposition, mainly into ammonia and water.

The comparatively feeble basic reaction of an aqueous solution of ammonia is traceable to this tendency to decomposition, and not to lack of ionization of the ammonium hydroxide¹. In the neutral reaction of its salts with strong acids, such as the chloride and nitrate, and in the alkaline reaction of those with weak acids, exemplified by the carbonate and cyanide, the radical ammonium displays complete analogy with the metals potassium and sodium. This fact constitutes a strong argument in favour of the view that ammonium hydroxide, so far as it is present in an aqueous solution of ammonia, is to a great extent ionized.

The formation of an ammonium amalgam, the general character of the ammonium salts, the existence of the monohydrate, the electrochemical properties of aqueous solutions of ammonia, and the similarity of the quaternary ammonium bases to the hydroxides of sodium and potassium, justify the consideration of the ammonium compounds in conjunction with those of the alkali metals.

¹ Compare Schlubach and Ballauf, *Ber*, 1921, 54, [B], 2825.

to 212° , then it may be inferred that the real expansion of water from greatest density by 170° is $\frac{1}{5}$ of its volume, so that the absolute expansion of water is determinable this way, without knowing either at what temperature its density is greatest, or the expansion of the vessel containing it

Cor 3 If the expansion of any vessel can be obtained, then may the temperature at which water is of greatest density be obtained, and *vice versa*. This furnishes us with an excellent method of ascertaining both the relative and absolute expansion of all solid bodies that can be formed into vessels capable of holding water

Cor 4 If the apparent expansion of water from maximum density for 180° were to be equalled by a body expanding uniformly, its velocity must be equal to that of water at 90° , or mid-way—And if any solid body be found to have the same expansion as water at 10° from max density, then its expansion for 180° must be $\frac{1}{9}$ of that of water, &c Because in water v is as t , &c

By graduating several glass thermometer vessels, filling them with water, exposing them to different temperatures, and comparing results, I have found the *apparent* expansion of water in glass for every 10° of the common

density of an atmospheric gas the less rapidly does the amount of it present diminish with increase in the height of the atmosphere

History—Hydrogen was known to the alchemists as a product of the interaction of acids and metals, and was called "inflammable air"

The suggestion first made by John Joachim Becher (1635–1682), that combustion is essential to chemical change, was further developed by Georg Ernst Stahl¹ (1660–1734). Stahl's theory involved a number of assumptions, which admit of the following summary

1 All combustible substances are compounds

2 Burning eliminates from these substances a constituent common to them all, "phlogiston" ($\phi\lambda\sigma\gamma\sigma\tau\sigma\tau\sigma$, burnt)

3 The degree of combustibility increases with the proportion of phlogiston present

4 Substances like phosphorus, carbon, sulphur, and many organic bodies contain a large proportion of phlogiston

5 Metals also contain phlogiston in varying proportions. They are to be regarded as compounds of this substance with the calx left after their combustion

6 The reconversion of metallic calxes into the metal by heating with carbon, gases, and other substances—in modern parlance the reduction of the oxide—is the result of a combination of the phlogiston of the reagent with the calx

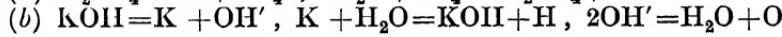
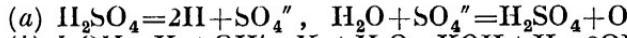
The phlogiston theory remained unrefuted for about fifty years. In 1772 Rutherford discovered nitrogen, and in 1774 Priestley isolated oxygen ("dephlogisticated air"). Between the years 1772 and 1788 Lavoisier made numerous investigations into the nature of combustion, his results leading him to the conclusion that there is no essential difference between respiration, combustion, and calcination.

In 1781 Cavendish and Watt proved water to be produced by the combustion of hydrogen. A repetition of their experiments in 1783 by Lavoisier and Laplace indicated that water contains 1 volume of oxygen and 1.91 volume of hydrogen. The interaction of red hot iron and steam, with liberation of free hydrogen and production of a calx of iron, was also observed by Lavoisier.

The discovery of the compound nature of water by Cavendish and Watt, and the results obtained by Lavoisier and his coadjutors in their investigations of the quantitative composition of this substance, rendered the phlogiston theory untenable. It had played a useful part as the first step to placing the science of chemistry on a rational basis, and it is interesting to note that both Priestley and Cavendish remained phlogistrians to the end.

Preparation—The choice of method for the preparation of hydrogen in the laboratory is decided by the degree of purity required in the gas, but by suitable means the product obtained by the interaction of a metal and an acid can be sufficiently purified for ordinary use.

1 One of the best methods for the preparation of pure hydrogen is the electrolysis of water containing sulphuric acid or potassium hydroxide to limit the conductivity. The acid or alkali plays an important part in the process, as indicated in the schemes.



¹ Stahl *Fundamenta Chymiae*, Norimbergae, 1723.

for 1804, Dr. Hope has given a paper on the contraction of water by heat in low temperatures (See also Nicholson's Journal, Vol. 12) In this paper we find an excellent history of facts and opinions relative to this remarkable question in physics, with original experiments There appear to have been two opinions respecting the temperature at which water obtains its maximum density, the one stating it to be at the freezing point, or 32° , the other at 40° Previously to the publication of the above essay, I had embraced the opinion that the point was 32° , chiefly from some experiments about to be related Dr Hope argued from his own experiments in favour of the other opinion My attention was again turned to the subject, and upon re-examination of facts, I found them all to concur in giving the point of greatest density at the temperature 36° , or mid-way between the points formerly supposed In two letters inserted in Nicholson's Journal, Vol 13 and 14, I endeavoured to shew that Dr Hope's experiments supported this conclusion and no other I shall now shew that my own experiments on the apparent expansion of water in different vessels, coincide with them in establishing the same conclusion

The results of my experiments, without

alkali and with an oxidizing-solution such as acidified potassium permanganate To remove arsenic, Reckleben and Lockemann¹ recommend passing the gas through a saturated solution of potassium permanganate or a 5–10 per cent solution of silver nitrate, or over cupric oxide, for use on the manufacturing scale they advise employing a solution of bleaching-powder

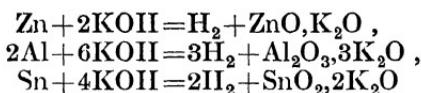
It is noteworthy that pure zinc decomposes dilute acids very slowly, but that addition of a few drops of a solution of cupric sulphate or platinum chloride greatly augments the velocity of the reaction A similar effect is produced by amalgamating the metal In both instances the acceleration is due to electrolytic action, the copper and platinum being deposited on the zinc (compare method 2, p 12)

For any metal the power of decomposing water and acids is determined by two factors the potential of the metal must be more negative, and its solution-pressure must be higher, than the corresponding constants of the hydrogen evolved from the water or dilute acid

Victor Meyer and von Recklinghausen² have pointed out that contact with hydrogen materially increases the tendency of potassium permanganate to evolve oxygen, so that in washing with this reagent there is risk of introducing oxygen as an impurity They explain the slow absorption of hydrogen by potassium permanganate by assuming oxidation to hydrogen peroxide, which is then decomposed by the permanganate with evolution of oxygen

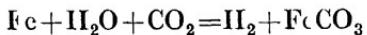
An improved type of generator for producing hydrogen from zinc and an acid has been described by Edwards³ It is said to be superior to the ordinary Kipp apparatus in rapidity of furnishing a supply of hydrogen free from air

5 Solution of zinc, aluminium, and tin in concentrated caustic alkalies evolves hydrogen, with formation of the zincate, aluminate, and stannate of the alkali metal



6 Hydrogen is evolved from aqueous solutions of strong reducing-agents, such as chromous salts,⁴ potassium cobaltocyanide,⁵ chloro molybdenum chloride⁶ (Mo_3Cl_6), and from all reducing agents with a reduction potential higher than that of hydrogen The velocity of the gaseous evolution is considerably accelerated by addition of finely divided platinum or palladium, especially from chromous chloride⁷

7 Bruno⁸ has prepared hydrogen by igniting iron filings with water saturated with carbon dioxide, the operation lasting 20–40 hours



Manufacture of Hydrogen -- Several methods are employed in the preparation of hydrogen on the large scale

¹ Reckleben and Lockemann *Zeitsch angew Chem* 1908 21 433
Victor Meyer and von I. *Ber* 1896, 29 2549, 2828

² Edwards *J Ind Eng* 1901 1 961

³ Berthelot *Compt rend* 1898 127 24

⁴ Peters *Pharm Centralhalle* 1898 39 695 Munchot and Herzog *Ber* 1900 33 1742

⁵ Muthmann and Nagel *Ber* 1898 31 2012

⁶ Peters *Zeitsch physikal Chem* 1898 26 193

⁷ Bruno *Bull Soc chim*, 1907, [4] 1 661

$\frac{1}{17.5}$ or rather more than 18 times as much; therefore the mean velocity of the expansion of water (which is that at 90°, or half way) is 18 times more than that of glass, which is equal to the expansion of water at 42°; this last must therefore be $\frac{1}{18}$ of the former, consequently water of 42° has passed through $\frac{1}{18}$ of the temperature to the mean, or $\frac{1}{18}$ of 90° = 5°, of new scale = 4° of old scale, above the temperature at which it is absolutely of greatest density This conclusion however cannot be accurate, for, it appears from the preceding paragraph that the temperature must be below 38° The inaccuracy arises, I have no doubt, from the expansion of glass having been under-rated by Smeaton, not from any mistake of his, but from the peculiar nature of glass Rods and tubes of glass are seldom if ever properly annealed, hence they are in a state of violent energy, and often break spontaneously or with a slight scratch of a file tubes have been found to expand more than rods, and it might be expected that thin bulbs should expand more still, because they do not require annealing, hence too the great strength of thin glass, its being less brittle, and more susceptible of sudden transitions of temperature From the above experiments it seems that the expansion due to glass, such

results by Dr George C Simpson in Captain Scott's last Antarctic expedition (1910-1912). In a modified form¹ of this process, the hydride is mixed with sodium hydrogen carbonate, boric acid, or soda-lime, and heated at 80° C. Namias² has pointed out that the use for balloons of hydrogen evolved from sulphuric acid and cast iron involves damage to the envelopes, the arsine and phosphine present becoming oxidized to arsenic acid and phosphoric acid respectively, and these acids exert a corrosive action on the material of the gas-bag. Jorissen³ has given a useful summary of the methods employed in the preparation of gas for balloons.

3 Jaubert⁴ described a process involving the use of "hydrogenite," a mixture of silicon, calcium hydroxide, and sodium hydroxide. At red heat it reacts in accordance with the equation



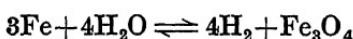
This method is also employed for balloon-gas.

4 At red heat calcium carbide reacts with water-vapour, liberating hydrogen and carbon dioxide⁵



The carbon dioxide is absorbed by lime. The yield is excellent, the hydrogen produced is very pure, and is well adapted for heating and lighting, and for filling balloons.

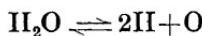
5 Lavoisier's work on the composition of water showed that steam reacts with iron at 150° C., liberating hydrogen and forming ferroso-ferric oxide, Fe_3O_4 .



Deville⁶ investigated the reaction, and proved it to be reversible. The proportion of hydrogen in the equilibrium mixture is greatest at 800° C.,⁷ a higher temperature shifting the equilibrium to the left, and causing reduction of the iron oxide. Deville believed the composition of the solid phase to correspond with the formula Fe_4O_5 , but later work by Preuner⁸ leaves it still undecided between Fe_3FeO , $\text{FeO}_2\text{Fe}_3\text{O}_4$, and $\text{Fe}_2\text{Fe}_3\text{O}_4$.

The interaction of steam and iron takes place in three stages⁹

(1) Dissociation of steam



(2) Combination of the nascent oxygen with the iron to form ferrous oxide



After one hour at 350° C. this reaction becomes perceptible.

¹ Bünziger Bock and Wenz German Patent 1910 No 218257
Namias *J. Industria Chimica* 1907 7, 257

² Jorissen *Chem Weekblad* 1911 8, 625

³ Jaubert *Rev gen Chim* 1910 13, 341, 357

Siemens and Halske German Patent 1910 No 220486

⁶ Deville *Compt rend* 1870 70, 1105, 1201, 71, 30 *Annalen* 1871 157, 71

⁷ Tittermann *J. Gasbeleuchtung* 1896, 39, 187, 204

⁸ Preuner *Zeitsch physikal Chem* 1904 47, 385

⁹ Friend *J. West of Scotland Iron and Steel Inst* 1910, 17, 66 *J. Iron and Steel Inst* 1909 II, 172 Friend, Hull and Brown, *Trans Chem Soc* 1911 99, 969 Chaudron *Compt rend*, 1914, 154, 237 Friend *The Corrosion of Iron and Steel* (Longmans 1911) chap III. Further details are given in this series Vol IX, Part II

whereas Smeaton makes it more. The vessel was made of the patent malleable zinc of Hodson and Sylvester. Perhaps it contains a portion of tin, which will account for the deviation.

Lead expands $\frac{1}{175}$ of its bulk for 180° ; water therefore expands about $5\frac{1}{4}$ times as much, this gives $90 - 5\frac{1}{4} = 16\frac{1}{4}$ of new scale = 13° of old scale, whence $49^\circ - 13^\circ = 36^\circ$, as before.

From these experiments it seems demonstrated, that the greatest density of water is at or near the 36° of the old scale, and 37° or 38° of the new scale and further, that the expansion of thin glass is nearly the same as that of iron, whilst that of stone ware is $\frac{1}{2}$, and brown earthen ware $\frac{1}{4}$ of the same.

The apparent expansion of mercury in a thermometrical glass for 180° I find to be 0163 from 1 That of thin glass may be stated at 0037 = $\frac{1}{175}$, which is rather less than iron, $\frac{1}{85}$. Consequently the real expansion of mercury from 32° to 212° is equal to the sum of these = 02 or $\frac{1}{5}$. De Luc makes it, 01836, and most other authors make it less because they have all under rated the expansion of glass. Hence we derive this proportion, 0163 : 180° :: 0037 : 41 nearly, which expresses the effect of the expansion of glass on

The behaviour of hydrogen at very low pressures has been investigated by Rayleigh¹. At about 15 mm it obeys Boyle's law, and continues to do so within very narrow limits up to 150 mm.

Holborn² has studied the isotherms of hydrogen at 0° C., 50° C., and 100° C., the pressure limits being 20 and 100 atmospheres. As unit of pressure he selected that of a column of mercury having a height of one mètre at 0° C under the normal gravity, $g=980\ 665 \text{ cm} \cdot \text{sec}^2$, and the unit of volume was the volume of the gas under this pressure. Within the limits of experimental error, amounting to a few parts in ten thousand, the isotherms for 50° C and 100° C were linear, whilst the deviation of that for 0° C did not exceed one part per thousand. The results obtained can be expressed in the following formulae

$$\begin{aligned} 0^\circ \text{ C } & pv = 0\ 99918 + 0\ 00082094p + 0\ 0000003745p^2, \\ 50^\circ \text{ C } & pv = 1\ 18212 + 0\ 00089000p, \\ 100^\circ \text{ C } & pv = 1\ 36506 + 0\ 00091400p \end{aligned}$$

Expressed as functions of $\frac{1}{v}$, the formulæ are

$$\begin{aligned} 0^\circ \text{ C } & pv = 0\ 99918 + (0\ 00081613)/v + (0\ 000001220)/v^2, \\ 50^\circ \text{ C } & pv = 1\ 18112 + (0\ 0010505)/v + (0\ 000001015)/v^2, \\ 100^\circ \text{ C } & pv = 1\ 36506 + (0\ 0012450)/v + (0\ 000001240)/v^2 \end{aligned}$$

The effect of pressure on hydrogen is represented graphically in fig 1 (p 18), the product pv being plotted³ against the pressure p . Neon and helium resemble hydrogen in being less compressible than Boyle's law demands⁴.

Travers⁵ observed that at ordinary temperature the expansion of hydrogen without doing work is attended by rise of temperature, indicating that under these conditions it behaves as an "ultra perfect" gas, at -80° C and 200 atmospheres its effusion without doing work is unaccompanied by calorific effect, a property characteristic of a perfect gas. Dewar⁶ found that at -200° C hydrogen begins to assume the character of an imperfect gas, expansion without external work being attended by fall in temperature. Lundolt⁷ gives the diffusion coefficient of hydrogen with respect to oxygen as 0.677 sq cm sec at 0° C and 760 mm.

Hydrogen is absorbed by wood charcoal, and Kasper⁸ has shown that 1 cc of this substance at 0° C and 130 mm absorbs 1.5 cc, at the same temperature and 1800 mm it absorbs 11.7 cc.

Lohfeldt⁹ gives for the electrochemical equivalent of hydrogen 96,590 coulombs or 0.17,11 million cc of gas per coulomb. The

¹ Rayleigh *Phil Trans* 1901 196 205 1902, 198 417 1905 204 351 *Proc Roy Soc* 1905 [A] 74 446

² Holborn *Ann Physik* 1920 [4] 63, 674

³ Fig 1 is taken from this series Vol I 29. In that volume comparative details of the behaviour of other gases under pressure are given.

⁴ Compare this series Vol I Part II

⁵ Travers *Phil Mag* 1901 [6] 1 411

⁶ Dewar *Chem News* 1896 73 40

⁷ Landolt-Bornstein and Meyerhofer *Tabellen* 3rd ed Berlin 1905 375

⁸ Kasper *Wied Annalen* 1881 12 526

⁹ Lohfeldt *Phil Mag* 1908 [6] 15 614

ing these observations, it is remarkable how nearly those liquids approximate to the law of expansion observed in water and mercury. Few authors have made experiments on these subjects, and their results in several instances are incorrect. My own investigations have been chiefly directed to water and mercury; but it may be proper to give the results of my enquiries on the other liquids as far as they have been prosecuted.

Alcohol expands about $\frac{1}{7}$ of its bulk for 180° , from — 8 to 172° . The relative expansions of this liquid are given by De Luc from 32° to 212° , but the results of my experiments do not seem to accord with his. According to him alcohol expands 35 parts for the first 90° , and 45 parts for the second 90° . The strength of his alcohol was such as to fire gun-powder but this is an indefinite test. From my experiments I judge it must have been very weak. I find 1000 parts of alcohol of 817 sp gravity at the temperature 50° became 1079 at the temperature 170° of the common mercurial scale. At 110° the alcohol is at 1039, or half a division below the true mean. When the sp gravity is 86, I find 1000 parts at 50° become 1072 at 170° , at 110° the bulk is 1035+, whence the disproportion of the two parts of the scale is not so much

Croullebois¹ has determined the refractive indices at ordinary temperature and pressure for the C, E, and G lines of the solar spectrum Merton and Barratt² have studied the spectrum of hydrogen

Liquefaction—The fact that hydrogen cannot be liquefied solely by pressure engendered a belief in the impossibility of its liquefaction In 1877 Cailletet³ allowed hydrogen at a pressure of 280 atmospheres to expand adiabatically to the pressure of the atmosphere, whereupon the temperature dropped below -200°C , and a fine, transient mist of hydrogen appeared Olszewski⁴ confirmed Cailletet's results, and by the aid of liquid air as a cooling-agent Dewar⁵ effected complete liquefaction He cooled the gas to -205°C at a pressure of 180 atmospheres, and then allowed it to expand to atmospheric pressure, collecting the condensed hydrogen in a double walled vacuum-flask, silvered to retard absorption of heat On the initiative of Travers⁶ and of Olszewski,⁷ the principle of Linde's air-liquefier has been utilized in the construction of a machine for the liquefaction of hydrogen on the large scale, the gas being first cooled to -200°C

In the liquid state hydrogen is colourless and transparent, and a non-conductor of electricity Although its surface-tension is low, being $\frac{1}{35}$ that of water and $\frac{1}{5}$ that of liquid air, it has a distinct meniscus and drops well It obeys the law of Dulong and Petit, its specific heat⁸ being about 6 Its atomic volume at the boiling-point is 14.8, and its density is 0.07, or $\frac{1}{14}$ of that of water⁹ Its density at -252.83°C and 745.52 mm is 0.07105¹⁰ The latent heat of evaporation at the boiling-point is 123.1 cal¹¹ Dewar¹² gives the boiling point at atmospheric pressure as -252.5°C , or 20.5° abs Olszewski¹³ gives -252.6°C , and for the critical temperature -240.8°C , and for the critical pressure 13.4–15 atmospheres The value calculated by Goldhammer¹⁴ for the critical density is 0.02748 Travers and Jacquierod¹⁵ have tabulated the values obtained by them for the vapour-pressure

¹ Croullebois *Ann Chim Phys* 1870 [4] 20 136

Merton and Barratt, *Phil Trans*, 1922, [A] 222, 369

³ Cailletet *Compt rend* 1877 85, 851 *Ann Chim Phys* 1878 [5] 15 132

⁴ Olszewski *Compt rend* 1885 101 238

⁵ Dewar *Trans Chem Soc* 1898 73 528 *Chem News* 1900 81 136 For a general account of the liquefaction of gases see this series Vol I 39 to 42

⁶ Lewis *Phil Mag* 1901 [6] 1 411 *Zeitsch physikal Chem* 1901 37 100
The Study of Gases (Macmillan 1901)

⁷ Olszewski *Ann Chim Phys* 1903 [7] 29 289 *Bull Acad Sci Cracow* 1902 619
1903 211

⁸ Dewar *Proc Roy Soc* 1901 [A] 68 360

⁹ Dewar *Trans Chem Soc* 1898 73 528

¹⁰ Augustin *Ann Physiol* 1915 [1] 46 419

¹¹ Dewar *Proc Roy Soc* 1905 [A] 76 325

¹² Dewar *ibid* 1901 [A] 68 44 360

¹³ Olszewski *Drude's Annalen* 1905 17 986 *Bull Acad Sci Cracow* 1908 375

¹⁴ Goldammer *Zeitsch physikal Chem* 1910 71 577

¹⁵ Travers and Jacquierod *Chem News* 1902 86 61

least 8 per cent. water, it is fair to infer from the above that a thermometer of pure alcohol would in no apparent degree differ from one of mercury in the interval of temperature from 50° to 170° . But when we consider that the relative expansions of glass, mercury and alcohol for this interval, are as 1, 5 $\frac{1}{2}$ and 22 respectively, it must be obvious that the inequality of the expansion of glass in the higher and lower parts of the scale, which tends to equalise the apparent expansion of mercury, has little influence on alcohol, by reason of its comparative insignificance. Hence it may be presumed that a spirit thermometer would be more equable in its divisions than a mercurial one, in a vessel of uniform expansion. This it ought to be by theory, because the point of greatest density or congelation of alcohol is below that of mercury.

Water being densest at 36° , and alcohol at a very remote temperature below, it was to be expected that mixtures of these would be densest at intermediate temperatures, and those higher as the water prevailed, thus we find the disproportion, so observable in the expansion of water, growing greater and greater in the mixtures as they approach to pure water.

Water saturated with common salt expands as follows 1000 parts at 32° become 1000

variation of the experiment is to fill the tube with nitrogen, which is superior to air because of its inertness towards hydrogen, on heating it in an atmosphere of hydrogen, diffusion inwards causes a rise in the pressure of the gas within the tube

Sieverts¹ observed that at high temperatures copper-wire, iron-wire, nickel, cobalt, and platinum² occlude hydrogen, but that silver does not (p 294). He found that diffusion through copper begins at 640° C, through iron³ at 300° C, and slowly through nickel at 450° C, but that there is no diffusion through silver at 640° C. Sieverts's⁴ results also indicate the insolubility of the gas in cadmium, thallium, zinc, lead, bismuth, tin, antimony, aluminum, gold, tantalum, and tungsten, but Heald⁵ states that most freshly precipitated metals absorb hydrogen.

Metals permitting the passage of hydrogen at a red heat, but not of other gases, may be regarded as having the character of a semi-permeable membrane. Palladium is the most permeable of these metals, Graham⁶ having found that a sheet with a thickness of 1 mm allows 327 c.c. to pass per sq. cm in one minute at 265° C, and 3992 c.c. at 1062° C. The fact that the velocity of diffusion, although dependent on the pressure, does not decrease proportionally with it, is cited by Winkelmann⁷ as an argument in support of his theory of the atomic condition of hydrogen occluded by palladium⁸.

Many metals occlude hydrogen, and there is a close connexion between their power of occlusion and their magnetic properties⁹. At the ordinary temperature, elements with a specific magnetic susceptibility exceeding 0.9×10^{-6} occlude hydrogen readily, but, as a general rule, other elements lack this capacity.

The amount of hydrogen occluded by metals depends on the pressure, and diminishes with rise of temperature. It is also affected by the physical condition and previous history of the metal. Mond, Ramsay, and Shields¹⁰ found that at ordinary temperature and 1 to 4.6 atm. the absorption of hydrogen by palladium black is 878 vols., and between these limits is independent of the pressure. For spongy palladium the absorption is 852 vols., and for palladium foil previously heated to redness, 816 vols. Most of the occluded gas is evolved in vacuum at the ordinary temperature and the residual 2-8 per cent. at that of boiling sulphur. At different stages of the occlusion the heat evolved is the same, being 4.370 cal. for each gm. of hydrogen. At ordinary temperatures spongy platinum absorbs 110 vols. of hydrogen, variations of pressure between 0.5 and 1.5 atm. producing little effect on the amount occluded.

¹ Sieverts *Zeitsch physikal Chem.* 1907 60 129. With respect to nickel compare Meyer und Altmeier *Ber.* 1908 41 3062. Sieverts und Hagenacker *Ber.* 1909 42 338. *Zeitsch physikal Chem.* 1909 68 115.

² Compare Neinst und Lessing *Cottinger Nachrichten* 1902 146. Gutbier und Musch *Ber.* 1919 52 [B] 1368. Schmidt und Lücke *Zeitsch Physik* 1921 8 152.

³ Schmidt und Lücke *loc. cit.*

⁴ Sieverts und Krumhahn *Ber.* 1910 43 593. *Zeitsch physikal Chem.* 1910 74 277. Sieverts *Zeitsch Elektrochem.* 1910 16 707. Sieverts and Boigner, *Ber.* 1911 44 2394.

⁵ Heald *Physikal Zeitsch.* 1907 8 659.

⁶ Graham *Proc Roy Soc.* 1867 15 227. 1868 16 422. 1869 17 212. 500.

⁷ Winkelmann *Drude's Annalen* 1901 6 104. Ramsay *Phil Mag.* 1894 38 206.

⁸ See this series Vol. IX Part I 176.

⁹ D. P. Smith *J. Physical Chem.* 1919 23 186.

¹⁰ Mond, Ramsay and Shields *Proc Roy Soc.* 1897 62, 290. *Zeitsch anorg Chem.*, 1898 16, 325. *Zeitsch physikal Chem.*, 1898 25, 657.

—36° or below; whence it accords with the same law as water and mercury. I find that even the glacial sulphuric acid, or that of 1 78 sp. gravity, which remains congealed at 45°, expands uniformly, or nearly like the other, whilst it continues liquid.

Nitric acid, sp. gravity 1 40, expands about 11 per cent from 32° to 212°; the expansion is nearly of the same rate as that of mercury, the disproportion not being more than 27 to 28 or thereabouts. The freezing point of acid of this strength is near the freezing point of mercury.

Muriatic acid, sp. gravity 1 137, expands about 6 per cent from 32° to 212°, it is more disproportionate than nitric acid, as might be expected, being so largely diluted with water. The ratio is nearly 6 to 7.

Sulphuric ether expands after the rate of 7 per cent for 180° of temperature. I have only compared the expansion of this liquid with that of mercury from 60° to 90°. In this interval it accords so nearly with mercury that I could perceive no sensible difference in their rates. It is said to freeze at —46°.

From what has been observed it may be seen that water expands less than most other liquids, yet it ought to be considered as having in reality the greatest rate of expansion.

Palladium-black contains both amorphous and crystalline palladium, and the proportion of each constituent and the sorptive capacity of the substance vary with the conditions of preparation. At low temperatures the sorptive capacity of palladium-black depends on the temperature at which sorption begins. When a sample saturated with hydrogen at 100° C is cooled in the gas, it sorbs more hydrogen. From 100° to 20° C the sorptive capacity decreases slightly, and increases continuously from 20° to -190° C. By heating palladium-black it is possible to increase the proportion of the crystalline variety¹. The relationship between the occlusive power of palladium for hydrogen and the activity of the metal for catalytic hydrogenation has been investigated by Maxted².

The occlusion of hydrogen by palladium decreases very rapidly with rise of temperature from 100° to 600° C, more slowly up to 800° C, and only very slightly between 800° and 1500° C³.

The effect of "poisons" on the occlusion of hydrogen by palladium has been studied by Maxted⁴. Hydrogen sulphide diminishes the occluding power of the metal, each atom of sulphur rendering almost exactly four atoms of palladium incapable of occluding the gas, while the remaining palladium occludes normally. de Hemptinne⁵ found that carbon monoxide deprives palladium of its sorptive power for hydrogen at low temperatures. Paal and Hartmann⁶ proved that carbon monoxide inhibits the activity of palladium for the catalytic reduction of sodium picrate, and observed⁷ mercury to exert a similar effect on palladium hydrosols.

A volumetric method for the estimation of hydrogen, either alone or in gaseous mixtures, is based by Paal and Hartmann⁸ on sorption by colloidal palladium, a simple gas-pipette being employed.

The occlusion of hydrogen by various metals has been investigated by Graham,⁹ and also by Neumann and Streintz¹⁰. Their results are appended in tabular form, and give the volume of hydrogen under normal conditions sorbed by one volume of the metal. It is noteworthy that their observation regarding silver is not confirmed by the more recent work of Sieverts.

Silver (wire)	0.21	Iron (reduced)	0.4-19.2
Silver (powder)	0.91 0.95	Magnesium	1.4
Aluminium (foil)	1.1 2.7	Nickel (reduced)	17-18
Cobalt (reduced)	5.9 15.3	Gold (leaf)	0.48
Copper (wire)	0.3	Gold (precipitated)	37-46
Copper (reduced)	0.6 4.5	Lead (fused)	0.11-0.15
Iron (wire)	0.16	Zinc	1.1-accs
Iron (malleable)	0.57 0.8		

¹ Firth *Trans. Chem. Soc.* 1921 119 1120

Maxted *ibid.* 225 1280

² Sieverts *Zeitsch. physikal. Chem.* 1911 88 103 451

³ Maxted *Trans. Chem. Soc.* 1919 115 1050 1920 117 1280

de Hemptinne *Zeitsch. physikal. Chem.* 1898 27 249

⁴ Paal and Hartmann *Ber.* 1910 43 243

⁵ Paal and Hartmann *Ber.* 1918 51 711; Paal and Steyer, *ibid.* 1743

⁶ Paal and Hartmann *Ber.* 1910 43 243 compare Brunel *Chem. Zeit.*, 1910,

⁷ Graham *Phil. Mag.* 1866 [1] 32 401 505 1874 [4] 47, 324

⁸ Neumann and Streintz, *Pogg. Annalen* 1839 46, 431

indicates it to be very low, or much lower than is commonly apprehended. Perhaps it may hereafter be demonstrated that the interval of temperature from 32° to 212° of Fahrenheit, constitutes the 10th, 15th, or 20th interval from absolute cold. Judging from analogy, we may conjecture that the expansion of solids is progressively increasing with the temperature, but whether it is a geometrical progression as elastic fluids, or one increasing as the square of the temperature, like liquids, or as the 3d or any power of the temperature, still if it be estimated from absolute cold, it must appear to be nearly uniform, or in arithmetical progression to the temperature, for so small and remote an interval of temperature as that between freezing and boiling water. The truth of this observation will appear from the following calculation let us suppose the interval in question to be the 15th, then the real temperature of freezing water will be 2520° , the mid-way to boiling 2610° , and boiling water 2700° , reckoned from absolute cold.

$\overline{14^{\circ}} = 196$	Dif	$\overline{14^{\circ}} = 2744$	Dif
$\overline{14\frac{1}{2}^{\circ}} = 210\frac{1}{2}$	$-\overline{14\frac{1}{2}^{\circ}}$	$\overline{14\frac{1}{2}^{\circ}} = 304\frac{1}{2}$	$-\overline{304\frac{1}{2}}$
$\overline{15^{\circ}} = 225$	$-\overline{15^{\circ}}$	$\overline{15^{\circ}} = 337\frac{1}{2}$	$-\overline{326\frac{1}{2}}$

to the ready inflammability of mixtures of the gas and air. During the war it was found possible to develop the production of helium within the British Empire on a commercial basis, and to employ this gas as a safe substitute for hydrogen in connexion with warfare in the air.¹ Within certain limits it has been found practicable to utilize non-inflammable mixtures of helium and hydrogen for this purpose. Such mixtures have the advantage of possessing a greater lifting power than pure helium. Ledig² found that a jet of helium with more than 14 per cent of hydrogen can be ignited in air, but that in balloon practice from 18 to 20 per cent of hydrogen can be employed, as the mixture does not burn with a persistent flame. With a proportion of hydrogen exceeding 20 per cent, the mixture is unsafe for use in war aeronautics.

von Wartenberg and Sieg³ found that the union of hydrogen and oxygen between 600° and 1000° C is attended by the formation of a considerable proportion of hydrogen peroxide, this product rapidly decomposing into water and oxygen. Ozone is formed by condensation of a part of the oxygen. The velocity of decomposition of the ozone being less than that of the hydrogen peroxide, a greater proportion of ozone is found in the mixture. Fiesel⁴ states that with moist hydrogen and oxygen the reaction is bimolecular, and that hydrogen peroxide may be an intermediate product, with the absolutely dry gases the reaction is termolecular.

The combination of hydrogen and nitrogen under pressure was effected by Le Chatelier⁵ in 1901, but owing to an explosion the method was not worked commercially. In 1905 the subject was further studied by Haber and van Oordt,⁶ who found that at red heat the velocity of combination is too slow to admit of measurement, and that at higher temperatures the amount of ammonia formed is small, either on account of rapid dissociation or because the reaction-affinity is small.

In 1910 Haber⁷ found that in presence of metallic osmium 1 volume of nitrogen unites with 3 volumes of hydrogen at 550° C and 200 atmospheres, the yield being 8 per cent of the mixed gases. On the manufacturing scale, osmium can be replaced by the less costly uranium, and a continuous circulation method is employed, with a temperature about 500° C.⁸ Any carbon monoxide present in the hydrogen should be removed.⁹

Methods for producing ammonia from its elements under the influence of the silent discharge and of the electric spark have not proved commercially successful.¹⁰

The other members of the nitrogen group do not form hydrides by

¹ Compare McLennan *Trans. Chem. Soc.* 1920, 117 923
Leditz *J. Ind. Eng. Chem.* 1920, 12 1098

² von Wartenberg and Sieg, *loc. cit.* 1920, 53 [B] 2192

³ Fiesel *Zeitsch. physikal. Chem.* 1921, 97 158

⁴ Le Chatelier *French Patent* 1901 No. 313950. *Compt. rend.* 1917, 164 588

⁵ Haber and van Oordt *Zeitsch. anorg. Chem.* 1905, 44 341

⁶ Haber *Zeitsch. Metallchem.* 1910, 16 241

⁷ Compte Claude *Compt. rend.* 1922, 174 681

⁸ Lumb, Seddon and Edgell *J. Inst. Chem. Soc.* 1922, 44, 738

⁹ Compte Muller and Giseinberger *British Patent* 1879 No. 1481. 1879 No. 1592. *Young British Patent* 1880 No. 1700. *Societe d'Azote German Patent* No. 17070. *Nithic German Patent* No. 95532. *West Deutsche Thomasphosphitwerke, German Patents* Nos. 157257 and 179300. *Gothanoff French Patent* No. 368585. *Hooper U.S. Patent* No. 791194. *Cassell German Patent* No. 175480. *Brenei and Mettler, Compt. rend.*, 1907, 144 694. *Davies Zeitsch. physikal. Chem.*, 1908, 64 657

certain temperature ; then 1000 cubic inches of the same will become 1003 by the same temperature

The following Table exhibits the expansion of the principal subjects hitherto determined, for 180° of temperature, that is, from 32° to 212° of Fahrenheit. The bulk and length of the articles at 32° are denoted by 1

EXPANSION		
SOLIDS	In bulk	In length.
Brown earthen ware.....	0012 = $\frac{1}{80}$	$\frac{1}{760}$
Stone ware	0025 = $\frac{1}{40}$	$\frac{1}{360}$
Glass—rods and tubes.....	0025 = $\frac{1}{40}$	$\frac{1}{360}$
— bulbs (thin)	0037 = $\frac{1}{20}$	$\frac{1}{180}$
Platinum	002 = $\frac{1}{50}$	$\frac{1}{450}$ †
Steel	0034 = $\frac{1}{25}$	$\frac{1}{225}$ †
Iron	0038 = $\frac{1}{22}$	$\frac{1}{198}$ †
Gold	0042 = $\frac{1}{18}$	$\frac{1}{162}$ *
Bismuth	0042 = $\frac{1}{33}$	$\frac{1}{297}$ †
Copper	0031 = $\frac{1}{65}$	$\frac{1}{585}$ †
Brass	0035 = $\frac{1}{56}$	$\frac{1}{504}$ †
Silver	0040 = $\frac{1}{25}$	$\frac{1}{225}$ *
Fine Pewter	0008 = $\frac{1}{125}$	$\frac{1}{125}$
Tin	0074 = $\frac{1}{13}$	$\frac{1}{130}$ †
Lead	0040 = $\frac{1}{25}$	$\frac{1}{225}$ †
Zinc	0093 = $\frac{1}{10}$	$\frac{1}{90}$ †
LIQUIDS		
Mercury	0200 = $\frac{1}{5}$	
Water	0400 = $\frac{1}{2}$	
Water sat with salt	0300 = $\frac{1}{3}$	†
Sulphuric acid	0600 = $\frac{1}{5}$	
Muriatic Acid	0600 = $\frac{1}{7}$	
Oil of turpentine	0700 = $\frac{1}{7}$	
Ether	0700 = $\frac{1}{8}$	
Fixed oils	0400 = $\frac{1}{2}$	
Alcohol	0110 = $\frac{1}{9}$	
Nitric acid	0110 = $\frac{1}{9}$	
PLASTIC FLUIDS.		
Gases of all kinds	370 = 1	

† Smecaton

* Ellicott

‡ Borda

Gaseous substances also react with hydrogen occluded by metals, the increased activity being probably due to the existence of the hydrogen partly in the atomic state and partly as hydride. The combination of hydrogen with the halogens and oxygen is promoted by the catalytic action of platinum and palladium, the same effect being noted by Kuhlmann¹ for the interaction of hydrogen and nitric oxide to form ammonia. The direct combination of nitrogen and hydrogen is not induced by these catalysts. It is noteworthy that hydrogenation cannot be induced by either the spongy or colloidal form of platinum or palladium completely freed from oxygen,² and that hydrogen desorbed from these metals retains activity for some time.³

A most important method for the application of hydrogen as a reducing agent has been discovered and elucidated by the researches of Sabatier and Senderens⁴. A very succinct summary of their work and that of other investigators has been given by Sabatier⁵. The method is simple, and consists in passing a mixture of the gaseous substance and hydrogen through a tube containing the finely divided metallic catalyst, obtained by previous reduction of the oxide in the same tube. For each reaction there is a suitable temperature, sometimes that of the atmosphere, but more usually 150° to 200° C. The neighbourhood of 180° C has been found well adapted for many reactions. The metals employed have been platinum-black, nickel, cobalt, iron, and copper. Of these catalysts nickel is the most active,⁶ and shares with cobalt the power of inducing reactions not promoted by the other metals. Copper is the least useful of the five, platinum and iron occupying an intermediate position.

The preparation of the catalyst can be exemplified by a description of the operations involved in the case of nickel. Unglazed biscuit-ware, broken to the size of peas, and freed from iron by boiling for several days with dilute hydrochloric acid, is rendered more porous by heating to redness for half an hour. After immersion in a concentrated solution of nickel nitrate, and evaporation of the liquid, the material is dried at 100° C., and subsequently heated until evolution of oxides of nitrogen ceases.



The reduction to metal is effected in the hydrogenation apparatus, the oxide being placed in a hard glass tube 1 metre long, and with a bore of 2 cm, supported in a slanting position, and surrounded by an iron tube having holes drilled in it for the insertion of thermometers. The hydrogen employed is washed successively with an acid solution of potassium permanganate, concentrated sodium hydroxide, and concentrated sulphuric acid, and finally passed over heated, palladized asbestos. During the operation the temperature of the reduction tube is maintained at 300° C., the end of the reaction being indicated by cessation in the production of water.

¹ Kuhlmann *Innalen* 1839 **29** 272

Willstatter und Waldschmidt *Lieb. Ber.* 1921 **54** [B] 113

² Anderson *Trans. Chem. Soc.* 1922 **121**, 113; compare Chittcock and Tyndall *Phil. Mag.* 1908 [6] **16**, 21; Usher *Trans. Chem. Soc.* 1910, **97**, 400; Collie and Patterson, *Proc. Chem. Soc.* 1913 **29**, 22; 117, 1 and, *J. Amer. Chem. Soc.* 1919 **41**, 545; Wendt *ibid.* 1920 **42**, 930.

³ Sabatier und Senderens *Compt. rend.* 1897 **124** 1358, 1899, **128** 1173, 1900 **130** 1761 **131** 40, 1901 **132** 1254 **133** 321, 1902 **134** 514 **135** 225.

⁴ Sabatier, *Ber.* 1911 **44** 1984.

⁵ See this series, Vol. IX Part 1, 95.

pages, there is reason to think these numbers are much too large.

The following Table exhibits some of the more remarkable temperatures in the whole range, according to the present state of knowledge.

	We
Extremity of Wedgwood's thermometer.....	24
Pig iron, cobalt and nickel, melt from 130° to.....	15
Greatest heat of a Smith's forge	15
Furnaces for glass and earthen ware, from 40 to	15
Gold melts	3
Settling heat of flint glass	2
Silver melts	2
Copper melts	2
Brass melts	2
Diamond burns	1
Red heat visible in day-light
	Fahrenhei old scale
Hydrogen and charcoal burn 300° to	100
Antimony melts	80
Zinc ..	70
Lead	61
Mercury boils	60
Linseed oil boils	60
Sulphuric acid boils	59
Bismuth ..	47
Tin	44
Sulphur burns slowly ..	30
Nitric acid boils	24
Water and essential oils boil	21
Bismuth 5 parts, tin 3 and lead 2, melt	210

activity of the evolved hydrogen depends on the pressure at which it is discharged at the cathode

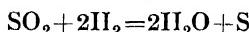
Zenghelis¹ proved the chemical activity of hydrogen to be much increased by bringing the gas in very minute bubbles into contact with solutions. His process consisted in forcing the gas into paper cartridges under such conditions as to inhibit bubbling through the paper, but so as to facilitate reaction with the dissolved substance in the pores of the cartridge. At 90° C an appreciable reduction of mercuric chloride to mercurous chloride was observed, and between 80° and 85° C a similar reduction of potassium chlorate to potassium chloride. Contact for three days at the ordinary temperature, and more rapidly at 65° C, yielded evidence of the conversion of carbon dioxide into formaldehyde and substances with characteristic sugar properties. At ordinary temperature, potassium nitrate was reduced to potassium nitrite, and under similar conditions of temperature an experiment lasting half an hour transformed sufficient nitrogen into ammonia to give the Nessler test.

The energy characteristic of the nascent state is attributed by Zenghelis to the very fine state of division of the reacting gas.

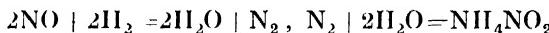
Reduction of Metallic Oxides—Hydrogen can displace many metals from their oxides, the reduction taking place at the ordinary temperature, as with silver and palladium oxides, or on heating, as with the oxides of copper, cadmium, lead, antimony, nickel, cobalt, and iron. Sometimes these reductions are incomplete, an equilibrium being attained. Such equilibria depend on the experimental conditions, an example being the action of steam on heated iron (p. 15).

Rasching² observed that a mixture of hydrogen and nitrogen peroxide passed through a heated tube reacts with such violence as to cause explosion.

The influence of the silent electric discharge on mixtures of hydrogen and other gases has been studied by Losanitch³. Sulphur dioxide is rapidly reduced, with liberation of sulphur.



Nitric oxide reacts fairly rapidly, forming ammonium nitrite. Two stages may be assumed:



At ordinary temperature pure hydrogen slowly reduces concentrated sulphuric acid to sulphur dioxide and water.⁴ Carbon disulphide forms a brown insoluble solid of the formula $3\text{CS}_2\text{H}_2$. Acetylene produces a light yellow mass containing two substances, one is a thick liquid with the formula $(\text{C}_2\text{H}_2)_2$, is soluble in ether and has a pleasant odour, the other is an insoluble solid $(2\text{C}_2\text{H}_2\text{C}_2\text{H}_4)$, of pungent odour and high molecular weight.

Triatomic Hydrogen Papers on the reactivity of hydrogen prepared by the electrolysis of dilute sulphuric acid have been published by Osann.⁵ The special reactivity of the gas was proved by Lowenthal⁶ to be due to the presence of sulphur dioxide derived from the sulphuric acid.

¹ Zenghelis *Compt. rend.* 1920, 170, 883.

Rasching *Zeitsch. angew. Chem.* 1907, 20, 694.

³ Losanitch *Ber.* 1907, 40, 4656.

⁴ Jones *Mem. Manchester Phil. Soc.* 1917, 61, No. 3, 1.

⁵ Osann, *J. prakt. Chem.* 1853, 58, 385; 1854, 61, 500; 1855, 56, 102; 1856, 69, 1.

1857, 71, 355; 1859, 78, 93; 1860, 81, 20; 1864, 92, 210.

⁶ Lowenthal *J. prakt. Chem.* 1858, 73, 116.

denoted by 1 and 04 nearly; because we have to divide .5 by 13 6, the specific gravity of mercury

That bodies differ much in their specific heats, is manifest from the following facts

1 If a measure of mercury of 212° be mixed with a measure of water of 32°, the mixture will be far *below* the mean temperature.

2 If a measure of mercury of 32° be mixed with a measure of water of 212°, the mixture will be far *above* the mean

3 If two equal and like vessels be filled, the one with hot water, the other with hot mercury, the latter will cool in about half the time of the former

4 If a measure of sulphuric acid be mixed with a measure of water of the same temperature, the mixture will assume a temperature about 240° higher

These facts clearly shew that bodies have various affinities for heat, and that those bodies which have the strongest attraction or affinity for heat, possess the most of it in like circumstances, in other words, they are said to have the greatest *capacity for heat*, or the greatest specific heat. It is found too that the same body changes its capacity for heat, or apparently assumes a new affinity, with a change of

of methyl acetate by a volumetric method Bredig and Fraenkel¹ have based an accurate volumetric method of determining the concentration of hydrogen ions on the catalytic decomposition of ethyl diazoacetate

Tolman² found for the transport-number of the hydrogen ion the value 0.184

A characteristic of the hydrogen ion is its tendency to form complex ions, yielding with ammonia the radical ammonium, NH_4^{\cdot} ³ and with the amines substituted ammonium radicals. The cation of the oxonium salts may be regarded as a complex ion formed by union of a neutral compound, such as ethyl ether, with the hydrogen ion. Dimethyl-pyron⁴ also yields complex hydrogen ions, other examples being the anions of the primary salts $\text{HSO}_4^{'}$, $\text{HF}_2^{'}$, $\text{HCO}_3^{'}$, $\text{HC}_2\text{O}_4^{'}$, and others⁵

References to the work of other investigators of the hydrogen ion are appended⁶

THE STRUCTURE OF ATOMIC NUCLEI

The problem of the constitution of atomic nuclei has been attacked from two opposite points of view. One method has consisted in attempting to synthesize nuclei heavier than the parent, the other has been concerned with the disruption of atomic nuclei.

The synthetic process is exemplified by the work of Collie and his coadjutors⁷ on the effect produced by exposing hydrogen at low pressure to the action of cathode rays. Many experiments under different conditions were made. In some of them the residual gas was found to contain varying proportions of helium and neon, in others the results were negative. It has been suggested that the presence of these gases might be due to contamination from the material of the apparatus or from the atmosphere, but the elaborate experimental precautions adopted make such an explanation untenable. Earlier work by Ramsay and by Collie⁸ had proved the presence of both helium and neon in the residual gases of old X-ray bulbs.

Sir J. J. Thomson⁹ tried the effect of cathode rays in experiments similar to those of Collie and Patterson and obtained not only helium and neon but also a considerable proportion of a gas denoted by him as X_3 . Thomson believed the helium and neon to have been evolved from the materials of the apparatus under the influence of the electric discharge, Collie and Patterson regarded these gases as having been

¹ Bredig and Fraenkel *Zeitsch Elektrochem.* 1905, **11**, 525. *Zeitsch physikal. Chem.* 1907, **60**, 202. ² Tolman *J. Amer. Chem. Soc.* 1911, **33**, 121.

³ Werner and Mielitz *Zeitsch physikal. Chem.* 1893, **12**, 35.

⁴ Walden *Ber.* 1901, **34**, 4183.

⁵ Abegg and Böhländer *Z. tech. anorg. Chem.* 1898, **20**, 475.

⁶ Ostwald *Lehrbuch der allgemeinen Chemie* Lipsia 1893, **2**, 1, 901 and 952. *Zeitsch physikal. Chem.* 1900, **35**, 333. Wilsmore *ibid.* 291. 302. Bosc *ibid.* 1900, **34**, 702. Wulf *ibid.* 1901, **48**, 87. Ostwald and Luther *Hand- und Hilfsbuch* 3rd ed. Lipsia 1910, 437. Neurath *Ber.* 1897, **30**, 1557. Tapworth *Trans. Chem. Soc.* 1908, **93**, 2187. Baly, Purdie and Masson *ibid.* 1909, **95**, 1096. Cathcart (*J. Ind. Eng. Chem.* 1922, **14**, 278) has described a simple hydrogen generator for use in making hydrogen ion determinations.

⁷ Collie and Patterson *Trans. Chem. Soc.* 1913, **103**, 419. *Proc. Chem. Soc.* 1913, **29**, 217. Collie *Proc. Roy. Soc.* 1914, [A], **90**, 554. Collie, Patterson and Masson *ibid.*, **91**, 30. compare Masson *Proc. Chem. Soc.* 1913, **29**, 233.

⁸ Ramsay and Collie *Nature* 1912, **89**, 502. Ramsay *Trans. Chem. Soc.*, 1913, **103**, 264. ⁹ Thomson *Nature*, 1913, **90**, 645.

with a view to obtain the true mean temperature

That water *increases* in its capacity for heat with the increase of temperature, I consider demonstrable from the following arguments : 1st. A measure of water of any one temperature being mixed with a measure at any other temperature, the mixture is less than two measures Now a condensation of volume is a certain mark of diminution of capacity and increase of temperature, whether the condensation be the effect of chemical agency, as in the mixture of sulphuric acid and water, or the effect of mechanical pressure, as with elastic fluids 2 When the same body suddenly changes its capacity by a change of form, it is always from a *less* to a *greater*, as the temperature ascends , for instance, ice, water and vapour 3 Dr Crawford acknowledges from his own experience, that dilute sulphuric acid, and most other liquids he tried, were found to increase in their capacity for heat with the increase of temperature

Admitting the force of these arguments, it follows that when water of 32° and 212° are mixed, and give a temperature denoted by 119° of the common thermometer, we must conclude that the true mean temperature is somewhere *below* that degree I have already

step If this conception be correct, a marked tendency towards the formation of elements with even atomic numbers would be anticipated Harkins has pointed out that there is actually a great predominance of elements of this type

Through his work on the mass spectra of the elements, Aston¹ is convinced that, with the exception of H₂ and H₃, all masses measured by him are whole numbers The conclusion is subject to the limits of experimental error, but is equally true of atomic, molecular, elementary, and compound masses Aston has obtained evidence of the existence of isotopes, believed by Harkins to account for the divergence of atomic weights from whole numbers Indications of the separation of chlorine into two isotopes have also been described by Harkins²

In Rutherford's earlier experiments on the disruption of nitrogen and oxygen by the particles of radium-C,³ he thought that both gases were capable of disintegration with expulsion of an atom of mass 3 His later investigations proved the method employed to fix the source of the radiation to be untrustworthy on account of the considerable variation in the thickness of films of metal foil The results obtained by a more direct and simple method indicated, at least for oxygen, that the particles originate in the radioactive source, and not in the volume of the surrounding gas In his view much experiment will be required to fix definitely the nature of the radiation, but the general evidence indicates it to consist of particles of mass 4 projected from the source, and to constitute a new mode of transformation of radium-C⁴

As a result of the insight respecting the inner constitution of atoms gained during the last twenty years, modern thought regards the atoms of all the different elements as having the same general type of structure The greater part of the mass of the atom is due to the presence at the centre of the atom of a positively charged nucleus of minute dimensions Around the nucleus is a region with a diameter of the order of 2×10^{-8} cm occupied by electrons maintained in equilibrium by the forces from the nucleus According to the law of Moseley, the resultant nuclear charge of an atom is equal to the atomic or ordinal number of that atom, varying from one "atom" of electricity for hydrogen to ninety two "atoms" for uranium, the ordinal numbers also representing the number of "planetary" electrons surrounding the atomic nucleus Except for mass, the ordinary physical and chemical properties of the atom depend entirely on the number and arrangement of the external electrons, that is, on the nuclear charge The mass of the atom is a property of the nucleus, its effect on the ordinary properties of the atom and on the distribution of the electrons being much less pronounced The production of atoms with the same nuclear charge but of different nuclear masses, known as isotopes, is explicable on this assumption

The removal of one or more of the external planetary electrons from the atom under the influence of electrical discharges or of light, or the elimination of one of the more strongly bound electrons by means of X-rays or β -rays, would effect a transformation of the atom of a temporary nature only, for its restoration to its original condition would

¹ F W Aston *Phil Mag*, 1920 [6] 39 611

² Harkins *Science* 1920 51 289 *Physical Review*, 1920, 15, 74, Harkins and Hayes, *J Amer Chem Soc* 1921 43 1803

³ Rutherford *Proc Roy Soc* 1920 [A] 97, 374

⁴ Rutherford *Trans Chem Soc*, 1922, 121, 400

Dr. Crawford, when investigating the accuracy of the common thermometer, was aware, that if equal portions of water of different temperatures were mixed together, and the thermometer always indicated the mean, this was not an infallible proof of its accuracy. He allows that if water have an increasing capacity, and the mercury expand increasingly with the temperature, an equation may be formed so as to deceive us. This is in fact the case in some degree, and he appears to have been deceived by it. Yet the increased capacity of water, is by no means sufficient to balance the increased expansion of the mercury, as appears from the following experiments.

I took a vessel of tinned iron, the capacity of which was found to be equal to 2 oz of water, into this were put 58 ounces of water, making the sum = 60 ounces of water. The whole was raised to any proposed temperature, and then two ounces of ice were put in and melted, the temperature was then observed, as follows.

thermometer twice as fast as water, though it has but half its capacity for heat, the times in which a thermometer is in cooling in fluids, are not, therefore, tests of their specific heats.

expressing the atomic weight of hydrogen by a fraction, and founded his table on the basis $O=100$. The standard $O=1$ was adopted by Meinecke in 1817, by Bischof in 1819, and also by Thomson.

Dalton formulated water as HO , but Berzelius considered that its formula should be H_2O , since it can be produced from two volumes of gaseous hydrogen and one volume of gaseous oxygen. Convinced of the impossibility of determining atomic weights accurately, Gmelin and his adherents in 1826 and later years advocated the adoption of a set of equivalents, that of hydrogen being taken as unity, and that of oxygen as 8 on the basis of Dalton's formula for water. According to Berzelius's view, the atomic weight of hydrogen compared with oxygen as 100 was 6.24, but in deference to the views of Gmelin he introduced the conception of double atoms, denoted by a horizontal line through the symbol of the element, the corresponding numbers being known as "Berzelius's atomic weights". In the table based on this compromise the ratio H/O was 12.48/100 in Berzelius's notation, or in round numbers 1.8 in that of Gmelin.

Experiments by Dumas and by Erdmann and Marchand in 1842 fixed the ratio H/O as 12.5/100 = 1.800, and it remained unaltered until 1860. In 1858–1860 Cannizzaro proposed adopting for oxygen the atomic weight $O=16$, and, in accordance with his suggestion, the atomic weights of a number of the elements were taken as double their equivalents. In 1860 Stas determined the atomic weight of hydrogen to be 1.005 ($O=8$), in terms of Berzelius's system, and in 1865 he gave the value as 1.0025 compared with $O=16$, in accordance with modern conceptions.

Although neither of these numbers agrees with the present accepted value, it is noteworthy that Stas was among the first to suggest employing $O=16$ as the standard, a system adopted by him almost exclusively in his published work. He did not utilize the standard $H=1$, beyond stating that in comparison with it the value for oxygen could not exceed 15.96, and giving a number of atomic weights calculated on this basis, but the atomic weight of hydrogen as unity proved very attractive, and was always employed by many chemists, although some adhered to Stas's table, calculated from $O=16$. In his book on atomic weights, published in 1882, Clark employed chiefly the values $H=1$ and $O=15.96$ as the basis of calculation, although he also used $O=16$ as standard. In a treatise on atomic weights, published in 1883, Lothar Meyer and Scubert adopted the ratio $H/O=1.1596$ but they also tried to introduce a system based on the value $O=1$.

In 1882 Stas announced a new value for the atomic weight of hydrogen, 1.01 ($O=16$) and in the following year Marignac¹ urged without success the adoption of Stas's original value $O=16$ as the standard. In 1885 Ostwald² criticized Stas's conclusion that the value $O=16$ necessitates for hydrogen a value higher than unity, and employed the ratio $H/O=1.16$ as the basis of his atomic weights.

Such was the condition of the subject in 1887, when the publication of results obtained by Cooke and Richards, and by Kaiscr, shed a new light on the matter. Their work, confirmed by that of Rayleigh and of Crafts, proved the ratio $H/O=1.1596$ to be inaccurate, and indicated

¹ Marignac, *Arch Sci phys nat*, 1883, 10, 5–27. *Oeuvres Complètes* Geneva 1902, 2, 714.

² Ostwald, *Lehrbuch der allgemeinen Chemie*, Leipzig, 1885, I, 44.

affinity for water, is to mix equal weights of water, and any proposed body of two known temperatures, and to mark the temperature of the mixture. Thus, if a pound of water at 32° , and a pound of mercury of 212° , be mixed, and brought to a common temperature, the water will be raised m degrees, and the mercury depressed n degrees; and their capacities or specific heats will be inversely as those numbers, or, $n : m \cdot \cdot \cdot$ specific heat of water : specific heat of mercury. In this way Black, Irvine, Crawford and Wilcke, approximated to the capacities of various bodies. Such bodies as have an affinity for water, may be confined in a vessel of known capacity, and plunged into water so as to be heated or cooled, as in the former case.

The results already obtained by this method are liable to two objections. 1st the authors presume the capacities of bodies while they retain their form are permanent, that is, the specific heat increases exactly in proportion to the temperature, and 2d, that the common mercurial thermometer is a true test of temperature. But it has been shewn that neither of these positions is warrantable.

The calorimeter of Lavoisier and Laplace was an ingenious contrivance for the purpose of investigating specific heat, it was calculated to

To correct the error caused by weighing in air, this value has been recalculated,¹ introducing a correction for vacuum, and the value H=6 2915 obtained The corresponding ratio is

$$\text{H O} = 1 \ 15\ 894 = 1\ 0067 \ 16,$$

a close approximation to the value accepted at the present day

In 1842, in co-operation with Stas, Dumas² repeated the work of Berzelius and Dulong, employing many precautions to ensure the purity of the materials Without applying any corrections, the value of the ratio found was

$$\text{H O} = 1 \ 15\ 958 = 1\ 0026 \ 16$$

Subtracting the weight of the water formed from the air dissolved in the dilute sulphuric acid employed to generate the hydrogen,³ Dumas obtained the ratio

$$\text{H O} = 1 \ 15\ 988 = 1\ 00012 \ 16$$

The ratio of the two equivalents is 1 8, from which the ratio of the atomic weights in accordance with modern views is

$$\text{H O} = 1 \ 16$$

This value was for many years adopted as the atomic weight Dumas's method has been subjected to searching criticism at various times Berzelius⁴ objected to it on the ground that the air employed to displace the hydrogen at the end of the experiment dissolved in the water formed, thus augmenting the value for the atomic weight of hydrogen, and diminishing that for oxygen Melsens⁵ pointed out that a similar error resulted from occlusion of hydrogen by the reduced copper, the weight of the oxygen being consequently too low The chief source of error in Dumas's method was the presence of occluded gases in the cupric oxide employed, a point noted by Richards and Rogers⁶ During reduction these gases were given up by the oxide, the consequent loss of weight being reckoned as oxygen, whereas part of it was due to other occluded gas The result, 15 96 to 15 99 (H=1), indicates too low a value for the atomic weight of hydrogen and too high for oxygen

In 1842 Erdmann and Marchand⁷ followed closely the lines marked out by the earlier work of Berzelius and Dulong, and especially that of Dumas The precautions taken and the sources of error overlooked were similar to those characteristic of Dumas's work In some of their experiments the copper oxide was prepared from metallic copper, and in others by heating copper nitrate From one set of four experi-

¹ Compare Clarke *A Recalculation of the Atomic Weights* 3rd ed (Smithsonian Miscellaneous Collections Washington 1910 54, No 3)

² Dumas *Ann Chem Phys* 1843 13 8 189

³ Compare Sebelen *Beitrage zur Geschichte der Atomgewichte* Brunswick 1884, 119

⁴ Berzelius *Lekrbuch der Chemie* 5th ed Dresden 1843-1848, 3 1183, compare Sebelen *Beitrage zur Geschichte der Atomgewichte* Brunswick 1884 120

⁵ Melsens compare Sebelen *ibid* 119

⁶ Richards and Rogers *Amer Chem J* 1893 15 567

⁷ Erdmann and Marchand *J prakt Chem*, 1842 26, 461

vessels of unequal bases. (See plate 1. Fig. 1). Supposing heat to be represented by a quantity of liquid in each vessel, and temperature by the height of the liquid in the vessel, the base denoting the zero or total privation of heat, then the specific heats of bodies at any given temperature, x , will be denoted by multiplying the area of the several bases by the height or temperature, x . Those specific heats too will be directly as the bases, or as the increments of heat necessary to produce equal changes of temperature.

Let w and W = the weights of two cold and hot bodies, c and C their capacities for heat at the same temperature (or the bases of the cylinders), d = the difference of the temperature of the two bodies before mixture, reckoned in degrees, m = the elevation of the colder body, and n = the depression of the warmer after mixture, (supposing them to have no chemical action), then we obtain the following equations

$$1 \quad m + n = d$$

$$2 \quad m = \frac{W C d}{w c + W C}$$

$$3 \quad C = \frac{w c m}{W n}$$

basis for ascertaining the atomic weight of hydrogen. His mean result, recalculated with the atomic weights Ag=107.880, Cl=35.457, Br=79.916, and N=14.010, gives the ratio

$$\text{H O}=1 \ 15.793=1.0131 \ 16$$

The value for hydrogen thus obtained was too high, in contrast with the low ratios previously published by Stas.

By oxidation of a known volume of hydrogen, van der Plaats¹ in 1886 obtained a mean value corresponding with the ratio

$$\text{H O}=1 \ 15.95=1.003 \ 16$$

The investigation of Cooke and Richards,² begun in 1882, marks the opening of a new era in the history of the determination of the atomic weight of hydrogen, and after the application of necessary corrections the results yield a value identical with that obtained by Morley (p. 41) in 1895. The hydrogen employed was prepared from zinc and hydrochloric acid, by electrolysis of dilute hydrochloric acid with a zinc-amalgam anode, or by the action of aluminium on potassium hydroxide, and so purified by contact with potassium hydroxide, calcium chloride, sulphuric acid, and phosphorus pentoxide that spectroscopic tests failed to reveal the presence of any extraneous substance. The hydrogen was weighed directly, and oxidized by copper oxide prepared from pure electrolytic copper, the water formed being absorbed by phosphorus pentoxide and weighed, all weighings being reduced to vacuum. It was noted by Mendeleeff,³ and later by Agamennone,⁴ that the volume of an evacuated glass globe is diminished by atmospheric pressure, and at the suggestion of Lord Rayleigh⁵ a correction for this diminution was introduced by Cooke and Richards⁶ into their calculation, the hydrogen having been weighed in an elongated, cylindrical glass flask. The ratio obtained was

$$\text{H O}=1 \ 15.869=1.00826 \ 16$$

An observation of Mendeleeff⁷ that a change of pressure of one atmosphere produces a corresponding change in the volume of water, suggested to Brauner⁸ the necessity for applying a further correction to the calculation of Cooke and Richards, to eliminate an error introduced by their method of determining the capacity of their glass vessel. The ratio as recalculated by Brauner is

$$\text{H O}=1 \ 15.879=1.00762 \ 16$$

The method employed by Keiser⁹ in 1887 involved weighing hydro-

¹ van der Plaats *Ann Phys Chem* 1886, [6] 7 529

² Cooke and Richards *Proc Amer Acad* 1887 23 149 *Amer Chem J* 1888 10 81

³ Mendeleeff *The Elasticity of Gases* (Russian ed.) 1875 I §§ 85 and 86 p. 218

⁴ Agamennone and Bonatti *Atti R Accad Nazca* 1885 [4] I 665 699

⁵ Rayleigh *Proc Roy Soc* 1888 43 356

⁶ Cooke and Richards, *Proc Amer Acad* 1888 23, 182, *Amer Chem J* 1888, 10 191

⁷ Mendeleeff *The Weight of a Litre of Air* (Russian ed.), 1894, I 57

⁸ Brauner, Abegg and Auerbach's *Handbuch der anorganischen Chemie*, Leipzig, 1908,

² 1 20

⁹ Keiser, *Ber* 1887, 20, 2323

heat or cold produced : then the quantity of heat in both bodies will be $= (c w + CW) x$
 $= (w + W) M x \pm (w + W) M n.$

$$9 \text{ and } x = \frac{(w + W) M n}{(c w + CW) \text{ or } (w + W) M}$$

It is to be regretted that so little improvement has been made for the last fifteen years in this department of science. Some of the earliest and most incorrect results are still obtruded upon the notice of students, though with the least reflection their errors are obvious. I have made great number of experiments with a view to enlarge, but more especially, to correct the Tables of Specific Heat. It may be proper to relate some of the particulars. For liquids I used an egg shaped thin glass vessel, capable of holding eight ounces of water, to this was adapted a cork, with a small circular hole, sufficient to admit the stem of a delicate thermometer tube, which had two small marks with a file, the one at 92° , and the other at 82° , both being above the cork, when the cork was in the neck of the bottle, the bulb of the thermometer was in the centre of the internal capacity. When an experiment was made the bottle was filled with the proposed liquid, and heated a little

the mean value for the atomic weight in the first series being 1 00850, and in the second 1 00848

Leduc,¹ in 1892, also synthesized water by oxidizing hydrogen with cupric oxide, the mean of two experiments giving the ratio

$$\text{H O=1 15 88=1 0075 16}$$

The classical research of Morley,² a masterpiece of skill, ingenuity, and patience, carried out by a master of experimental method, consisted of four parts. In the first he determined the weight of a normal litre of oxygen, in the second the value of the same constant for hydrogen, in the third the relative proportions by volume in which, under normal conditions, hydrogen and oxygen unite to form water, and in the fourth the amount of water formed by the union of weighed quantities of oxygen and hydrogen. The methods of the first three parts are considered on pp 47 to 49, since they are of a physico-chemical nature, the fourth part involves a gravimetric process, and is accordingly described here.

In Morley's experiments the weight of oxygen contained in two globes was determined, and a quantity of hydrogen was weighed while absorbed in palladium. The two gases were combined, and the weight of water produced was ascertained. The gases were brought into contact at two platinum jets enclosed in a small glass apparatus (fig 2) previously exhausted and weighed. After the combination, the residual gas in the combustion chamber and the connecting tubes was extracted by means of a Toepler pump, measured, and analysed. The combustion chamber, the oxygen globes, and the palladium hydrogen tube were again weighed. The difference between the original weights of oxygen and hydrogen and those of the gases analysed gave the quantities combined in the combustion chamber. The gain in weight of the combustion chamber corresponded with the amount of water produced, and should have been equal to the sum of the weights of the gases consumed. The observed difference was due to experimental errors, and indicated the degree of accuracy of the operation.

In most of the experiments the volume of hydrogen employed was between 42 and 43 litres, and the weight of water produced was about 34 grams. The proportion of uncombined gas varied between one six hundredth and one ten thousandth of the total amount. Each synthesis was complete in about one hour and a half.

The gases entered the combustion chamber at the jets *a*, and combination was initiated by spiking across the gap between the wings *b*. The two tubes *bb* were filled with phosphoric anhydride kept in place by asbestos, the oxide serving to prevent the escape of any traces of water formed. The joints *cc* were ground to fit joints connecting the apparatus through other phosphoric anhydride tubes to the sources of oxygen and hydrogen. The tubes *bb* were sealed at *d* and *e*, notches indicating the points of subsequent fracture. The hooks at the ends of the apparatus facilitated the hydrostatic weighing for determining its volume.

¹ Leduc, *Compt rend.*, 1892, 115, 41. *Ann Chim Phys.* 1898 [7] 15, 48.

² Morley, *Smithsonian Contributions to Knowledge*, Washington 1895, 29, No. 980. An account of the gravimetric work is given in *Amer Chem J.*, 1895, 17, 269 and a description of the density measurements in *Zeitsch physikal Chem.*, 1895, 17, 87. Compare also Freund, *The Study of Chemical Composition* (Cambridge University Press, 1904).

not enter into consideration. But as the heat of that was proved to be equal to $\frac{1}{4}$ of an ounce of water, or to $\frac{1}{2}$ of an ounce measure of oil, it is evident we must consider the heat disengaged in the 1st experiment, as from 8 $\frac{1}{2}$ ounces of water, and in the last as from 9 $\frac{1}{2}$ ounce measures of oil. On this account the numbers below 29 will require a small reduction, before they can be allowed to represent the times of cooling of *equal bulks* of the different liquids, in the last experiment the reduction will be one minute, and less in all the preceding ones.

It may be proper to observe, that the above results do not depend upon one trial of the several articles, most of the experiments were repeated several times, and the times of cooling were found not to differ more than half a minute, indeed, in general, there was no sensible differences. If the air in the room was, in any case, a little above or below 52°, the due allowance was made.

I found the specific heat of mercury, by mixture with water, and by the time of its cooling in a smaller vessel than the above, to be to that of water of equal bulk, as, 55 to 1 nearly.

I found the specific heats of the metals and other solids after the manner of Wilcke and

bination of weighed quantities of ammonia and hydrogen chloride when passed together into water until the solution was almost neutral, the slight excess of ammonia being determined by titration. The result obtained does not accord with that of Morley.

Thomsen's second method¹ of investigation embodied a novel principle. Weighed quantities of aluminium were brought into contact with a solution of potassium hydroxide, and the evolved hydrogen dried and weighed, the results giving the value of the ratio H : Al. Another series of experiments was made, the evolved hydrogen being combined with oxygen, and the water formed weighed, the data obtained being employed to calculate the ratio O : Al. From the results of the two sets of experiments, the ratio of the atomic weights was calculated as

$$\text{H} \text{ O} = 1 \ 15\ 869 = 1 \ 00826 \ 16$$

In 1897 Thomsen² revised the results obtained in this research, introducing a correction for the reduction of volume accompanying the solution of the aluminium in the potassium-hydroxide solution. The amended ratio is

$$\text{H} \text{ O} = 1 \ 15\ 8685 = 1 \ 00829 \ 16$$

In 1898 Keiser³ caused a known weight of hydrogen occluded in palladium to combine with oxygen, and determined the weight of the resulting water, the whole process being carried out in one apparatus. The mean of four experiments gave the ratio

$$\text{H} \text{ O} = 1 \ 15\ 880 = 1 \ 00756 \ 16,$$

a close approximation to Morley's value (p. 42).

The principle of the investigation carried out by Noyes⁴ in 1907 was similar to that adopted by him in the research of 1889-1890 (p. 40), hydrogen being oxidized by copper oxide, and the water formed being weighed in the oxidation apparatus. Five series of experiments were made, but the results of the first were not employed in the final calculation, being vitiated by retention of water in the copper oxide. The mode of procedure was modified for each series of experiments, the mean of twenty-five observations giving the ratio

$$\text{H} \text{ O} = 1 \ 15\ 8751 = 1 \ 00787 \ 16$$

For convenience in comparison, the foregoing results are grouped in the following table.

¹ Thomsen *Ztsch anorg Chem* 1896 11 14

² Thomsen *ibid* 1897 15 447

³ Keiser *Imm Chem J* 1898 20 733

⁴ Noyes *J Amer Chem Soc*, 1907 29 1718 1908 30 4

TABLE OF SPECIFIC HEATS.

GASES			equal weights	oz. blks	SOLIDS.	
Hydrogen	-	-	21.40*	.003	Ice	-
Oxygen	-	-	4.75*	.006	Dried woods, and other vegetable substances, from .45 to	.65
Common air	-	-	1.79*	.008	Quicklime	-
Carbonic acid	-	-	1.05*	.002	Pit-coal (1.27)	.25
Azotic	-	-	.79*	.001	Charcoal	-
Aqueous vapour	-	-	1.55*	.001	Chalk	.27
LIQUIDS					Hydrat lime	.35
Water	-	-	1.00	1.00	Fine glass (2.87)	.19
Arterial blood	-	-	1.03*		Muriate of soda	.23
Milk (1.026)	-	-	.98		Sulphur	-
Carbonat. of ammon (1.035)	-	-	.96		Iron	.19
Carbouat. of potash (1.30)	-	-	.75		Brass	.12
Solut. of ammonia (9.48)	-	-	1.03		Copper	.11
Common vinegar (1.02)	-	-	.92		Nickel	.10
Venous blood	-	-	.89*		Zinc	.10
Solut. of common salt (1.197)	-	-	.78		Silver	.08
Solut. of sugar (1.17)	-	-	.77		Tin	.07
Nitric acid (1.20)	-	-	.76		Antimony	.06
Nitric acid (1.30)	-	-	.68		Cold	.03
Nitric acid (1.36)	-	-	.63		Lead	.04
Nitrate of lime (1.40)	-	-	.64		Hismith	.04
Sulph. acid and water, equal b	-	-	.52		Oxide s of the metals sur- pass the metals themselves, according to Crawford	
Muriatic acid (1.153)	-	-	.61			
Acetic acid (1.056)	-	-	.66			
Sulphuric acid (1.844)	-	-	.31			
Alcohol (85)	-	-	.76			
Ditto (817)	-	-	.70			
Sulphuric ether (76)	-	-	.66			
Spermaceti oil (47)	-	-	.52			
Mercury	-	-	.04			

Three years later Fourcroy, Vauquelin, and Seguin¹ observed during a prolonged experiment that 12570 942 cubic inches of oxygen and 26017 968 cubic inches of hydrogen, reduced to 14° C and 28 inches of mercury, combined to form 7249 grains of water. By direct weighing, a cubic inch of water was found to weigh 0 4925 grain, and of hydrogen 0 040452 grain. The combined weights of the two gases exceeded the weight of the water formed by 0 277 grain. It follows from the results that 1 part by weight of hydrogen combines with 6 17 parts of oxygen, giving the ratio

$$\text{H O=1 } 12\ 34$$

In 1803 John Dalton fixed the atomic weight of hydrogen as unity, and gave the ratio of the atomic weights of hydrogen and oxygen according to the custom of the day as H O=1 5 5, a value far wide of the mark. In view of the statements of Gay-Lussac and Humboldt that water was formed by the combination of 2 volumes of hydrogen with 1 volume of oxygen, and those of Cavendish and Lavoisier that oxygen was fourteen times as heavy as hydrogen, Dalton in 1808 substituted the ratio

$$\text{H O=1 } 7$$

The first calculation with any approach to accuracy was that of Wollaston² in 1814. From the combining volumes of hydrogen and oxygen as given by Gay-Lussac and Humboldt in 1805, coupled with Biot and Arago's determination of the densities of the two gases, Wollaston calculated the atomic weight of hydrogen to be 6 64 (O=100). Expressed in modern terms the ratio is

$$\text{H O=1 } 15\ 09=1\ 06\ 16$$

Although the hypothesis of Avogadro and Ampère as to the relation between the densities and molecular weights of gases was propounded in 1811, half a century elapsed before its acceptance by the chemical world. Gay-Lussac's Law of Volumes, enunciated in 1808,³ led Berzelius to the assumption that the densities of elementary gases are proportional to their atomic weights. Acting on this assumption, he and Dulong in 1821 determined the densities of hydrogen and oxygen, the results being referred to air as unity. For hydrogen the density was found to be 0 0688, and for oxygen 1 1026, the ratio being

$$\text{H O=1 } 15\ 9538=0\ 9984\ 16$$

This experiment gives as the atomic weight of hydrogen 0 9984 (O=16), a result in good accord with that obtained by the same investigators by gravimetric methods (p. 36).

Subsequent research proved that Gay Lussac's Law of Combining Volumes is not exact, but only an approximation,⁴ so that oxygen and hydrogen do not behave as perfect gases. For an accurate calculation of the relative values for the atomic weights of hydrogen and oxygen, it is therefore essential to know not only the relative densities of the

¹ Fourcroy, Vauquelin, and Seguin *Ann. chim.* 1791 [1] viii 230. Seguin *ibid.*, ix, 50; compare Scheele *Beiträge zur Geschichte der Atomgewichte* Brunswick 1884 115.

² Wollaston *Phil. Trans.* 1814 104, 20.

³ Compare this series, Vol I, 14.

⁴ Compare *ibid.*, 15.

sulphur, are remarkably low, and carry their character along with them into compounds, as oil, sulphuric acid, &c.

Water appears to possess the greatest capacity for heat of any pure liquid yet known, whether it be compared with equal bulks or weights; indeed it may be doubted, whether any solid or liquid whatever contains more heat than an equal bulk of water of the same temperature. The great capacity of water arises from the strong affinity, which both its elements, hydrogen, and oxygen, have for heat. Hence it is that solutions of salts in water, contain generally less heat in a given volume than pure water for, salts increase the volume of water as well as the density, and having mostly a small capacity for heat, they enlarge the volume of the water more than proportional to the heat they contribute.

Pure ammonia seems to possess a high specific heat, judging from the aqueous solution, which contains only about 10 per cent — If it could be exhibited pure in a liquid form, it would probably exceed water in this particular.

The compounds of hydrogen and carbon, under the characters of oil, ether and alcohol, and the woods, all fall below the two last mentioned, the reason seems to be, because charcoal is an element of a low specific heat.

density of oxygen, the values obtained being 0 06948 and 1 10506 The ratio of these densities is

$$D_H D_o = 1 \ 15\ 905 = 1\ 0060 \cdot 16$$

In 1892 Rayleigh¹ employed hydrogen and oxygen prepared by electrolysis As the mean of nineteen experiments with hydrogen and eleven with oxygen, he found the ratio of the densities to be

$$D_H D_o = 1 \ 15\ 882 = 1\ 00748 \cdot 16$$

In 1893 he determined the densities of the two gases relative to air, the ratio being

$$D_H D_o = 1 \ 15\ 8818 = 1\ 00744 \cdot 16,$$

a result almost identical with that found by him in the preceding year

In 1895 Morley² published an account of his researches -The gravimetric results of his investigations have already been considered on p 41, the physico-chemical sections are briefly summarized here The weight of a litre of oxygen at 0° C and 760 mm, reduced to sea-level in the latitude of 45°, was determined by three series of experiments involving nine, fifteen, and seventeen observations respectively, the mean value for each series being

- (1) 1 42879 ± 0 000051 grams
- (2) 1 42887 ± 0 000048 grams
- (3) 1 42917 ± 0 000048 grams

The mean value of the three series is

$$1\ 42900 \pm 0\ 000034 \text{ grams}$$

The oxygen was prepared from potassium chlorate

The weight of a litre of hydrogen at 0° C and 760 mm, reduced to sea level in the latitude of 45°, was determined by five series of experiments, the number of observations being fifteen, nineteen, eight, six, and eleven respectively The value obtained for each series was

- (1) 0 089938 ± 0 000007 gram
- (2) 0 089970 ± 0 000011 gram
- (3) 0 089886 ± 0 000019 gram
- (4) " " " gram
- (5) 0 089866 ± 0 000034 gram

The mean value of all the series is 0 089897, but Morley considered the results of the first and second series to be too high, owing to the presence of mercury vapour in the glass globe This source of error was eliminated in the other three series, the mean value calculated from them being 0 08987, " " " gram

These results give for the mean ratio of the densities of the two gases

$$D_H D_o = 1 \ 15\ 9002 = 1\ 00628 \cdot 16$$

¹ Rayleigh *Proc Roy Soc* 1892 50 448 1893 53 144 1900, 66 334

² Morley *Smithsonian Contributions to Knowledge* Washington 1895 29, No 980, pp 1-94 and 110-114, *Phil Mag*, 1904, [6], 7, 667, compare Guye *J Chim phys*, 1907, 5 215

I used contained 33 per cent pure acid; this acid therefore, in combining with water, expels much heat.

Quicklime is determined by Lavoisier and Crawford to be 22; I think they have underrated it I find quicklime to impart as much or more heat than carbonate of lime, when inclosed in a vessel and plunged in water, or when mixed with oil Hydrat of lime (that is, quicklime 3 parts and water 1 part, or dry slaked lime) is fixed at 28 by Gadolin it was 25 by my first experiments, but I since find I have underrated it The subject will be adverted to in a future section

SECTION 4

THEORY OF THE SPECIFIC HEAT OF ELASTIC FLUIDS

Since the preceding section was printed off, I have spent some time in considering the constitution of elastic fluids with regard to heat The results already obtained cannot be relied upon, yet it is difficult to conceive and execute experiments less exceptionable than those of Crawford It is extremely important

of the ratio by another method¹ The weight of a normal litre of detonating gas, prepared at 0° C by electrolysis of an aqueous solution of sodium hydroxide formed by dissolving the metal in water, was determined to be 0 535510 gram From this number, and the corresponding values for hydrogen and oxygen, the ratio of the combining volumes of hydrogen and oxygen was calculated, allowance being made for the slight excess of hydrogen always present after the explosion of detonating gas prepared at 0° C At N T P the ratio found was

$$V_H \quad V_O = 2\ 00269 \quad 1$$

Employing another method, Rayleigh² found the value

$$V_H \quad V_O = 2\ 0026 \quad 1$$

In 1916 a very accurate determination of the ratio was made by Burt and Edgar³ The hydrogen was prepared by the electrolysis of barium hydroxide, and the oxygen either by the same method or by heating potassium permanganate The measurements were made at N T P , and a slight excess of hydrogen was employed Five series of experiments gave the volume ratio

$$V_H \quad V_O = 2\ 00288 \quad 1$$

(c) *The Atomic Weight Ratio*

Of the foregoing data, the results of Morley and of Burt and Edgar are the most trustworthy Combining Morley's ratio for the relative densities of the gases with that for their combining volumes, the atomic weight of hydrogen (O=16) is given by the expression

$$\text{Atomic weight of hydrogen} = \frac{1\ 00628 \times 2\ 00269}{2} \\ = 1\ 00768$$

This result approximates closely to that obtained by Morley in his gravitational researches (p 42)

If Morley's values for the weight of 1 litre of hydrogen (0 089873 gram) and of oxygen (1 42900 gram) are employed, Burt and Edgar's ratio gives for the atomic weight of hydrogen

$$1\ 00772$$

Adopting Germann's⁴ more probable value for oxygen, 1 42905, the atomic weight of hydrogen becomes

$$1\ 00769,$$

which is probably the most accurate result hitherto obtained

Other methods of calculation yield figures supporting those of Morley They utilize the densities and other physical constants of hydrogen and oxygen, and are based on the purely physical methods

¹ Morley *Smithsonian Contributions to Knowledge* 1895 29, No 980

² Rayleigh *Proc Roy Soc* 1904 [A], 73 153

³ Burt and Edgar *Phil Trans* 1916 [A] 216, 393

⁴ Germann *J Chem phys* 1914 12 66

high, compared with equal weights of carbonic acid and aqueous vapour, and of azotic gas or *phlogisticated* air, as it was then called, under the idea of its being an opposite to oxygen or *dephlogisticated* air. Indeed his deductions respecting azotic gas, are not consistent with his experiments: for he makes no use of experiments 12 and 13, which are the only direct ones for the purpose, but he infers the heat of azotic gas from the observed difference between oxygen and common air. The result gives it less than half that of common air, whereas from the 13th experiment, scarcely any sensible difference was perceived between them. He has in all probability much underrated it, but his errors in this respect whatever they may be, do not affect his system.

When we consider that all elastic fluids are equally expanded by temperature, and that liquids and solids are not so, it should seem that a general law for the affection of elastic fluids for heat, ought to be more easily deducible and more simple than one for liquids, or solids — There are three suppositions in regard to elastic fluids which merit discussion.

1 *Equal weights of elastic fluids may have the same quantity of heat under like circumstances of temperature and pressure.*

The truth of this supposition is disproved

results of modern gravimetric analysis If Noyes's value for hydrogen is adopted in the calculations, high values for chlorine are obtained¹

In the opinion of Noyes, the most trustworthy value is the mean between his own and Morley's gravimetric result, H=1 00774, and this view is strongly supported by the work of Burt and Edgar, and by calculations made by the method of limiting densities

In 1898 the German Committee on Atomic Weights selected 1 01 as the atomic weight of hydrogen² In 1903 the International Committee on Atomic Weights altered³ the number to

$$H=1\ 008,$$

a value still recognized at the present time In this series of textbooks the value

$$H=1\ 00762$$

has been selected for the calculation of atomic weights

¹ Sources of error in atomic weight determinations are considered in several papers by Guye and his collaborators (*J. Chim. phys.*, 1916, 14, 25, 195, 204, 1917, 15, 60, 208, 360, 405 1918 16, 46)

² Report of the German Committee on Atomic Weights, *Ber.*, 1898, 31, 2761, compare *ibid.*, 1900, 33, 1847

³ Report of the International Committee on Atomic Weights, *Proc. Chem. Soc.*, 1903, 19, 2

its formation must therefore be exactly equal to the whole heat previously contained in the charcoal on this supposition, but the heat by the combustion of one pound of charcoal seems, at least, equal to the heat by the combustion of a quantity of hydrogen sufficient to produce one pound of water, and this last is equal to, or more than the heat retained by the water, because steam is nearly twice the density of the elastic mixture from which it is produced, it should therefore follow, that charcoal should be found of the same specific heat as water, whereas it is only about $\frac{1}{2}$ of it. Were this supposition true, the specific heats of elastic fluids of equal weights would be inversely as their specific gravities — If that of steam or aqueous vapour were represented by 1, oxygen would be 64, hydrogen 8 4, azote .72, and carbonic acid 46 — But the supposition is untenable

3 The quantity of heat belonging to the ultimate particles of all elastic fluids, must be the same under the same pressure and temperature

It is evident the number of ultimate particles or molecules in a given weight or volume of one gas is not the same as in another for, if equal measures of azotic and oxygenous gases were mixed, and could be instantly

relatively high solubility of its chloride in alcohol or a mixture of alcohol and ether. With triphyllite fusion is unnecessary, the mineral being soluble in acids.

The method most generally applied to the isolation of lithium is based on the decomposition of the fused chloride by electrolysis, modifications in practical details having been introduced by various experimenters. Bunsen and Matthiessen¹ passed the current from six Bunsen cells through the fused chloride contained in a porcelain crucible, with a carbon rod as anode and an iron wire as cathode. Troost employed a similar method. Guntz² mixed lithium chloride with potassium chloride, but his product contained 1-8 per cent of potassium. His current was 10 ampères at 20 volts, with a cathode of iron wire 3-4 mm in diameter. Borchers³ added chlorides of other alkali-metals and alkaline-earth metals and a small proportion of ammonium chloride, and employed a current density of 10 amperes per 100 sq cm. Tucker⁴ electrolyzed the chloride without the addition of other material.

To avoid contamination of the lithium with alkali-metals, Ruff and Johannsen⁵ employed a mixture of lithium bromide with 10-15 per cent of lithium chloride, which melts about 520° C. The Muthmann copper electrolytic cell was used, with two iron wires of 4 mm diameter as anode and a current of 100 ampères at 10 volts.⁶

Direct electrolytic preparation of lithium from aqueous solutions of its salts is not feasible, but can be effected when the salts are dissolved in organic solvents such as acetone and pyridine.⁷ A solution of lithium chloride in pyridine was electrolyzed by Kahlenberg⁸ with a cathode of sheet platinum or iron wire and a current density of 0.2-0.3 ampere per 100 sq cm. Patten and Mott⁹ found that amyl alcohol is a suitable solvent, provided the current density is sufficiently high to ensure the velocity of deposition of the metal being greater than that of its solution in the alcohol.

Winkler's¹⁰ suggestion to reduce the hydroxide with magnesium has been proved practicable by Warren¹¹. The reaction is very energetic.

Physical Properties—Lithium is a white metal with silver-like lustre. It remains untarnished in dry air,¹² but a freshly cut surface develops a yellow tinge if moisture is present. In extremely thin layers it is translucent, the transmitted light having a dark, reddish-brown colour.¹³ It is harder than cesium, rubidium, sodium, or potassium, but softer than lead, the degree of hardness on Rydberg's¹⁴ scale being 0.6. In ductility it resembles lead, and can be drawn into wire or rolled into thin

¹ Bunsen *Annalen* 1855 94 107

Guntz, *Compt rend* 1893 117 732

² Borchers *Zeitsch Elektrochem* 1894 1 361 1895 2 39

³ Tucker *J Amer Chem Soc* 1902 24 1024

⁴ Ruff and Johannsen *Zeitsch Elektrochem* 1906 12 186

⁵ Compare Guntz, *L'Industria Chimica* 1907 7 284

⁶ von Laszcynski *Ber* 1894 27 2285 *Zeitsch Elektrochem*, 1895 2 55 von

Laszcynski and von Gorski *ibid* 1898 4 290

⁷ Kahlenberg, *J Physical Chem* 1899 3 601

⁸ Patten and Mott, *ibid* 1904 8, 153

⁹ Winkler, *Ber*, 1890 23 46

¹⁰ Warren *Chem News*, 1896 74, 6

¹¹ Dafert and Miklauz, *Monatsh* 1910, 31, 981

¹² Dudley, *Amer Chem J*, 1892 14, 185

¹³ Rydberg, *Zeitsch physikal Chem*, 1900, 33, 353

position, or as it may now be called, proposition, is demonstrated.

Corol. 1. The specific heats of equal weights of any two elastic fluids, are inversely as the weights of their atoms or molecules.

2. The specific heats of equal *bulks* of elastic fluids, are directly as their specific gravities, and inversely as the weights of their atoms.

3. Those elastic fluids that have their atoms the most condensed, have the strongest attraction for heat, the greater attraction is spent in accumulating more heat in a given space or volume, but does not increase the quantity around any single atom

4 When two elastic atoms unite by chemical affinity to form one elastic atom, one half of their heat is disengaged When three unite, then two thirds of their heat is disengaged, &c And in general, when m elastic particles by chemical union become n , the heat given out is to the heat retained as $m-n$ is to n

One objection to this proposition it may be proper to obviate it will be said, an increase in the specific attraction of each atom must produce the same effect on the system as an increase of external pressure Now this last is known to express or give out a quantity of the absolute heat, therefore the former must

water and in various organic solvents, such as methyl and ethyl alcohol,¹ the lithium salts are highly dissociated. The electric conductivity of their dilute aqueous solutions has been investigated by Ostwald,² Franke,³ and Kohlrausch and Maltby.⁴ The electric conductivity of the lithium ion at 18° C is 38.4. References to other work on the properties of lithium salt-solutions are appended.⁵

Transmutation of Copper into Lithium.—The transmutation of the baser metals into gold was one of the chief aims of the alchemists. Although their labours proved fruitless as regards their immediate object, they laid the foundation of that scientific chemistry to which the modern industrial world owes a deep debt of obligation. In 1818 Faraday contemplated as a possibility the transmutation of the metals, for he said in a lecture delivered before the City Philosophical Society "To decompose the metals, to re-form them, and to realize the once absurd notion of transmutation—these are the problems now given to the chemist for solution."⁶

Interest in the subject was revived in 1907 by Ramsay's⁷ announcement of the development of spectroscopic quantities of lithium in solutions of cupric sulphate or nitrate exposed to the radium emanation. In control experiments made without the emanation no lithium was detected. Mme Curie and Mlle Gleditsch⁸ repeated Ramsay's experiments, employing vessels of platinum instead of glass, but failed to detect the development of even a trace of lithium. They attribute Ramsay's results to solution of lithium present in the glass of his apparatus. Mlle Gleditsch⁹ detected the presence of lithium in a sample of pitchblende from Joachimsthal, as well as in other radioactive minerals, but failed to find any simple relationship between the proportion of lithium and copper present in the minerals examined. The results¹⁰ are summarized in the table.

Mineral	Percentage of Copper	Percentage of Lithium	Ratio of Copper to Lithium
Joachimsthal pitchblende	1.2	0.00017	7059
Colorado pitchblende	0.15	0.00034	441
Carnotite	0.15	0.080	5
Chalcolite (Cornwall)	0.54	0.00011	491
Autunite	Nil	0.00083	
Thorite	Trace	0.0033	

¹ Compare Haber und Saal *Zeitsch Elektrochem* 1902 8 245

² Ostwald *Zeitsch physikal Chem* 1887 1 83

³ Franke *ibid* 1895 16 463

⁴ Kohlrausch and Maltby *Sitzungsber K Akad Wiss Berlin*, 1899 II 665

Kohlrausch *ibid* 1900 II 1002 1901 II 1026 1902, I 572

⁵ Tolman *J Amer Chem Soc* 1911 33 121 Patten and Mott *J Physical Chem*, 1904 8 153 Schlamp *Zeitsch physikal Chem*, 1894 14 273, Bredig *ibid*, 1894

I 3 262

⁶ Compare Hydrogen p 32

⁷ Ramsay *Nature* 1907 76 269 Cameron and Ramsay *Trans Chem Soc* 1907, 91, 1593 Ramsay *ibid* 1909 95 624

⁸ Curie and Gleditsch *Compt rend* 1908, 147 345

⁹ Gleditsch, *ibid* 1907 145 1148

¹⁰ Gleditsch, *ibid*, 1908 146 331 *Le Radium*, 1908, 5, 33, compare Ramsay and Cameron, *Compt rend* 1908, 146 456

order to compare them with that of water, we shall further assume the specific heat of water to that of steam as 6 to 7, or as 1 to 1 166

Table of the specific heats of elastic fluids

Hydrogen.....	9 382	Olefiant gas .. .	1 555
Azote.....	1 866	Nitric acid	491
Oxygen.... .	1 333	Carbonic oxide	777
Atmos air.. .	1 759	Sulph hydrogen	583
Nitrous gas	777	Muriatic acid.	424
Nitrous oxide .	549	Aqueous vapour	1 166
Carbonic acid .	491	Ether vapour	848
Ammon gas	1 555	Alcohol vapour	586
Carb hydrogen	1 333	Water	1 000

Let us now see how far these results will accord with experience. It is remarkable that the heat of common air comes out nearly the same as Crawford found it by experiment, also, hydrogen excels all the rest as he determined, but oxygen is much lower and azote higher. The principles of Crawford's doctrine of animal heat and combustion, however, are not at all affected with the change. Besides the reason already assigned for thinking that azote has been rated too low, we see from the Table, page 62, that ammonia, a compound

The results of their analyses of lithium chloride are

AgCl $\text{LiCl} = 100$ 29 5786, whence $L_1 = 6\ 940$,
 Ag $\text{LiCl} = 100$ 39 2992, whence $L_1 = 6\ 939$

A description of the determination of the first of these ratios is given in Volume I of this series of text-books, as an example of the refinements employed in modern atomic-weight research

Further evidence concerning the atomic weight of lithium was furnished by Richards and Willard in their synthesis of lithium perchlorate by evaporating lithium chloride with perchloric acid. The result obtained was

L1Cl = 100 150 968, whence **L1** = 6 936

In the foregoing calculations the modern values for the atomic weights of silver and chlorine have been employed, but the following calculation indicates the assumption to be unnecessary. Taking the composition of silver chloride to be that given by Richards and Wells,¹

Ag AgCl=100 132 867,

it follows that

$$\frac{\text{LiCl}}{\text{AgCl}} \times \frac{\text{AgCl}}{\text{Ag}} = \frac{\text{LiCl}}{\text{Ag}} = 0.295786 \times 1.32867 = 0.393002$$

The mean of this result and that found directly (0.392992) is 0.392997
Hence

$$\frac{40}{\text{LiCl}} \times \frac{\text{LiCl}}{\text{Ag}} = \frac{40}{\text{Ag}} = 1.50968 \times 0.392997,$$

$$= 0.593300,$$

$$= 64.107871$$

Accordingly, Ag=107 871, and Cl=107 871×0 32867=35 454 But

$$L_1 Cl = 64 - 1 \cdot 50968 = 42\ 393$$

Hence

$$L_1 = 42\ 393 - 35\ 454, \\ \quad = 6\ 939$$

The current table of the International Committee on Atomic Weights gives

L₁=6.94

Molecular Weight—Ramsay² found the lowering of the vapour pressure of mercury produced by dissolving lithium in that metal, and from his results calculated for the molecular weight of lithium the value 7.1, approximately the same as its atomic weight. A different result was obtained by Heycock and Neville³ by the cryoscopic method with sodium as solvent, their value being about four times the atomic weight, the discrepancy possibly arising from the susceptibility of lithium to oxidation.

Position of Lithium in the Periodic System — In accordance with the

¹ Richards and Wells *J Amer Chem Soc* 1905 **27** 459

² Ramsay, *Trans Chem Soc*, 1889 55 521.

³ Heycock and Neville, *ibid.*, 675

using the calorimeter of the above philosophie and to a notion that its results are not always to be depended upon. Much important information may, however, be obtained on the subject by the use of a very simple apparatus as will appear from what follows:

I took a bladder, the bulk of which, when extended with air, was equal to 30000 grains of water; this was filled with any combustible gas, and a pipe and stop-cock adapted to a tinned vessel, capable of containing 30C grains of water was provided, and its capacity for heat being found, so much water was put into it as to make the vessel and water together equal to 30000 grains of water. The gas was lighted, and the point of the small flame applied to the concavity of the bottom of the tinned vessel, till the whole of the gas was consumed, the increase of the temperature of the water was then carefully noted, whence the effect of the combustion of a given volume of gas, of the common pressure and temperature, in raising the temperature of an equal volume of water, was ascertained, excepting very small loss of heat by radiation, &c which this method must be liable to, and which probably does not exceed $\frac{1}{2}$ or $\frac{1}{3}$ th of the whole.

The mean results of several trials of different gases are stated below, when

the hydride The analogy between the physical constants and other physical properties of lithium hydride and those of the alkali-metal halides, and the liberation of lithium at the cathode and hydrogen at the anode during electrolysis, indicate the hydride to be a salt of hydrogen in its capacity as a weak acid¹

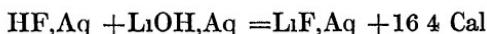
Lithium fluoride, LiF —The fluoride is obtained in granular form by concentrating a hydrofluoric-acid solution of the carbonate When crystallized from fused potassium chloride it forms regular octahedra, or leaflets with a mother-of-pearl lustre² Carnelley³ gives the melting-point as about 800° C, and Poulenc⁴ as about 1000° C, but Wartenberg and Schulz⁵ found 842° C The boiling point is 1676° C,⁶ and the vapour-pressure in atmospheres corresponds with the expression

$$\log p = -55100/4 \cdot 57T + 6 \cdot 190$$

The density of the fluoride is about 2.6

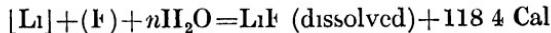
At 18° C 100 parts of water dissolve 0.27 part of lithium fluoride⁷ The salt is almost insoluble in alcohol of 95 per cent strength de Forcrand's⁸ value for the heat of solution is -1.04 Cal Its comparatively slight solubility constitutes a link with the fluorides of the alkaline-earth-metals (p. 54), and has been put forward as an argument in favour of the double formula Li_2F_2 , derived from the double molecule H_2F_2 , since the salts of lithium with monobasic anions are usually readily soluble If this view be correct, the analogy to the alkaline-earth metallic fluorides is rendered even more striking It is supported by the existence of lithium hydrogen fluoride, $\text{LiF}\cdot\text{HF}$, which crystallizes from a solution of the fluoride in hydrofluoric acid

Petersen⁹ has determined the heat of formation of lithium fluoride from the hydroxide in dilute aqueous solution



The heat of neutralization of strong acids and bases is usually about 13.7 Cal, and the enhanced value for lithium fluoride may be attributed to the heat evolved during neutralization by the ionization of the weak hydrofluoric acid

By combining the heat of neutralization given by the foregoing equation with the heats of formation of water, dissolved lithium hydroxide, and dissolved lithium fluoride, an equation is obtained giving the heat of formation of dissolved lithium fluoride from lithium, fluorine, and water



The heat of formation of the solid fluoride is unknown, since its heat of solution has not been determined

¹ Moers *Zeitsch anorg Chem* 1920, 113, 179

² Poulenc *Ann Chim Phys* 1894 [7] 2, 22

³ Carnelley *Landolt Bornstein and Roth's Tabellen* 4th ed Berlin 1912, 220

⁴ Poulenc *Ann Chim Phys* 1894 [7] 2, 22

⁵ von Wartenberg and Schulz *Zeitsch Elektrochem*, 1921, 27, 568, compare Albrecht and Wartenberg *ibid* 16, 2

⁶ von Wartenberg and Schulz *loc cit*

⁷ Mylius and Funk, *Ber* 1897, 30, 1716

⁸ de Forcrand *Compt rend* 1911, 152, 27

⁹ Petersen, *Zeitsch physikal Chem*, 1889, 4, 384

was ignited, then weighed, and the combustion was maintained by a gentle blast from a blow-pipe, directing the heat as much as possible upon the bottom of the vessel, after the operation it was again weighed, and the loss ascertained; the result never amounted to 2° for ten grains, but generally approached it nearly.

In order to exhibit the comparative effects more clearly, it may be proper to reduce the articles to a common weight, and to place along with them the quantity of oxygen known to combine with them. The quantity of heat given out may well be expressed by the number of pounds of ice which it would melt, taking it for granted that the quantity necessary to melt ice, is equal to that which would raise water 150° of the new scale. The results may be seen in the following table.

1lb hydrogen takes	7lbs oxygen, prod	8 lbs water melt	120lbs ice
— carbur hydrogen, 4	—	5 w & carb acid	85 —
— olefiant gas,	3 5 —	4 5 —	88 —
— carbonic oxide,	58 —	1 58 carb acid	85 —
— oil, wax and tallow	3 5 —	4 5 w & carb ac	104 —
— oil of turp	— — —	— — —	60 —
— alcohol,	— — —	— — —	58 —
— ether,	3 — —	4 — —	62 —
— phosphorus	1 5 —	2 5 pho. acid	60 —
— charcoal	2 8 —	3 4 carb acid	43 —
— sulphur	— — —	— — — sulph acid	20 —
— camphor	— — —	— — — w & carb ac	70 —
— caoutchouc	— — —	— — —	

(fig 3), the two breaks in the curve near 20° C and 100° C corresponding with the transition-temperatures of the individual hydrates. The three portions of the curve correspond with the solid phases $\text{LiCl}_2\text{H}_2\text{O}$, $\text{LiCl}_3\text{H}_2\text{O}$, and LiCl . The break on the dotted portion of the curve at -15° C represents the transition point of the trihydrate, $\text{LiCl}_3\text{H}_2\text{O}$. A saturated solution of the chloride in contact with the solid phase boils at 168° C^1 .

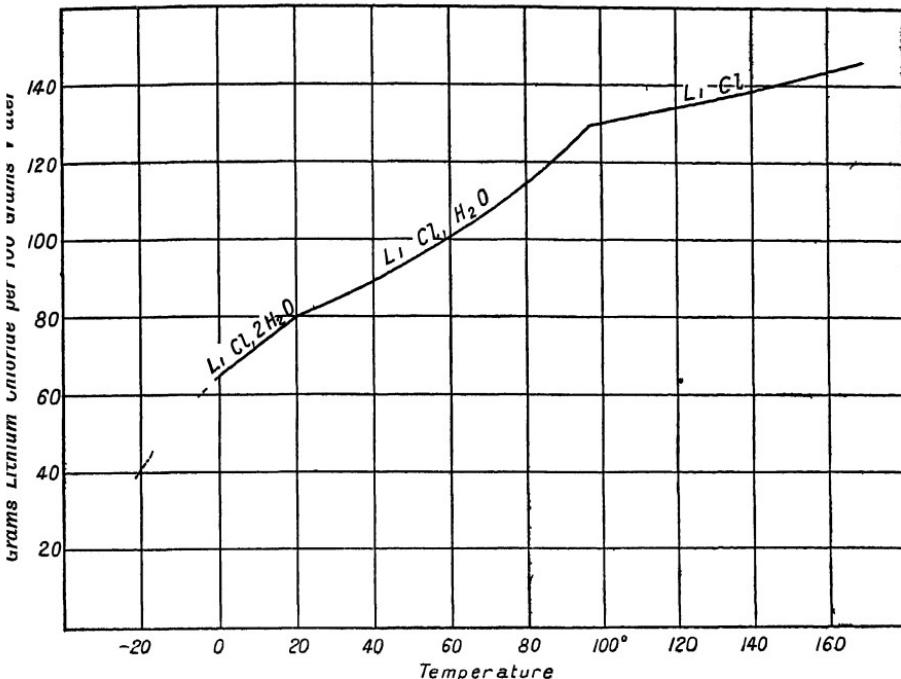


FIG. 3.—Solubility curve of lithium chloride

The solubility of lithium chloride has also been investigated by Gerlach,¹ whose results are given in the table.

Temperature ($^{\circ}\text{C}$)	0	10	20	30	40	50	60	80	100
Grams LiCl in 100 g. H ₂ O	67	72	78.5	84.5	90.5	97.0	103.0	115.0	127.5

References to work on the physical properties of aqueous solutions of lithium chloride are appended.²

Solutions of lithium chloride resemble water in their power of absorbing ammonia complex ammonia compounds being formed.³ The anhydrous lithium halides also absorb ammonia, Bonnefor⁴ having

¹ Gerlach *Zeitsch anal Chem* 1869 8 281

² Le Conte *Compt rend* 1897 125 603 Hosking *Phil Mag* 1904 [6] 7 469 Jongs and Götting *Zeitsch physikal Chem* 1903 46 269 Jahn *ibid* 1901 37 673 Wagner 1905 50 129 Biltz, *ibid* 1902 40 184 Arrhenius *ibid* 1887 1 295, Wagner 1890 5 31 Abegg *ibid* 1893 11 251 Öholm *ibid* 1905 50 309

³ Abegg and Riesenfeld *Zeitsch physikal Chem*, 1902, 40, 84, Dawson and McCrae, *Trans Chem Soc*, 1901, 79, 493

⁴ Bonnefor, *Ann Chim Phys*, 1901, [7] 23 317

Mine must necessarily be rather too low. But Lavoisier is in this as well as all the other articles, hydrogen excepted, unwarrantably too high. I think Crawford will be found too high, his experiments on the heat produced by the respiration of animals, support this supposition.

WAX AND OIL Crawford's results are a little lower than mine, which they ought not to be, and are doubtless below the truth Lavoisier's certainly cannot be supported This great philosopher was well aware of the uncertainty of his results, and expresses himself accordingly He seems not to have had an adequate idea of the heat of hydrogen gas, which contributes so much to the quantity given out by its combustion, he compares, and expects to find an equation between the heat given out by burning wax, &c and the heat given out by the combustion of equal weights of hydrogen and charcoal in their separate state, but this cannot be expected, as both hydrogen and charcoal in a state of combination must contain less heat than when separate, agreeably to the general law of the evolution of heat on combination —In fact, both Crawford and Lavoisier have been, in some degree, led away by the notion, that oxygenous gas was the sole or principal source of the light and heat pro-

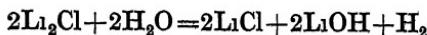
of formation of lithium chloride from its elements is expressed by the equation



The heat of solution in ethyl alcohol is 11.74 Cal,¹ in methyl alcohol 10.9 Cal.² The formation of compounds with alcohols has been investigated³ (see p. 62). At 25° C 100 grams of ethyl alcohol dissolve 25.83 grams of the salt.⁴

Lithium chloride forms double salts with the chlorides of other metals, such as copper,⁵ manganese,⁶ iron,⁶ cobalt,⁶ nickel,⁶ and uranium.⁷ With sodium chloride it forms a series of mixed crystals, but not with potassium chloride.⁸

Lithium subchloride, Li₂Cl—According to Guntz,⁹ lithium chloride is converted by lithium into a hard, greyish substance of the formula Li₂Cl. It decomposes water readily



Lithium bromide, LiBr—The anhydrous bromide is obtained by dissolving the carbonate in aqueous hydrobromic acid, and evaporating the solution to dryness in a current of gaseous hydrogen bromide. Bogorodsky¹⁰ has isolated three hydrates from the aqueous solution, each forming very deliquescent crystals. At very low temperatures the trihydrate, LiBr·3H₂O, is deposited, at 4° C it is changed to the dihydrate, LiBr·2H₂O, at 44° C this substance yields the monohydrate, LiBr·H₂O, above 159° C the anhydrous salt is deposited. A crystalline form is also described¹¹ containing 1-1½H₂O. For the melting-point of anhydrous lithium bromide Carnelley¹² gives 547° C, and Wartenberg and Schulz¹³ give 549° C, but Ramsay and Eumorfopoulos¹⁴ found the much lower value 442° C. At its melting-point it evolves bromine freely.¹⁵ The boiling-point is 1310° C,¹⁶ and the vapour-pressure in atmospheres corresponds with the expression

$$\log p = -35600/4.57T + 5.109$$

The values obtained by Kremers¹⁷ for the solubility in water are given in the table.

Temperature °C	0	10	20	30	40	50	60	80	100
Grams LiBr in 100 g. H ₂ O	113	161	177	190	202	214	224	245	266

¹ Pickering *Trans. Chem. Soc.* 1888 53 865

² Lemoine *Compt. rend.* 1897 125 603

³ Turner and Bissell *Trans. Chem. Soc.* 1914 105 1777

⁴ Turner and Bissell *ibid.* 1913 103 1904

⁵ Chassévant *Compt. rend.* 1891 113 646 Cambi *Gazzetta* 1909 39 1, 361

⁶ Chassévant *Compt. rend.*, 1892, 115, 113

⁷ Aloy *Bull. Soc. chim.* 1899 [3] 21 264, compare Liebisch and Korring *Sitzungsber. K. Akad. Wiss. Berlin* 1914, 192

⁸ Schaefer *Jahrb. Min. Bul. Bd.* 1919 43 132

⁹ Guntz *Compt. rend.* 1895 121 945

¹⁰ Bogorodsky *J. Russ. Phys. Chem. Soc.* 1893 25 316 1894 26 209

¹¹ Guarasci *Atti R. Accad. Sci. Torino* 1913 48 735

¹² Cunnelly *Fandoll Bonstain and Roth's Tabellen* 4th ed. Berlin 1912 220

¹³ von Wartenberg and Schulz *Zeitsch. Elcktrochem.* 1921, 27 568 compare Albrecht and von Wartenberg *ibid.* 162

¹⁴ Ramsay and Eumorfopoulos *Phil. Mag.*, 1896 41, 360

¹⁵ Guarasci *loc. cit.*

¹⁶ von Wartenberg and Schulz *loc. cit.*

¹⁷ Kremers *Pogg. Annalen*, 1858, 103, 57, 104, 133, 105 360

trary, in proportion to its specific heat before the combustion A similar observation may be made upon the heat produced by the union of sulphur with the metals, and every other chemical union in which heat is evolved.

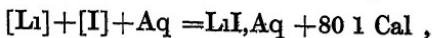
Before we conclude this section it may be proper to add, for the sake of those who are more immediately interested in the economy of fuel, that the heat given out by the combustion of 1lb of charcoal, and perhaps also of pitcoal, is sufficient (if there were no loss) to raise 45 or 50 lbs of water from the freezing to the boiling temperature , or it is sufficient to convert 7 or 8 lbs of water into steam If more than this weight of coal be used, there is a proportionate quantity of heat lost, which ought, if possible, to be avoided

SECTION 6

ON THE
NATURAL ZERO OF TEMPERATURE,
Or absolute Prinatice of Heat

If we suppose a body at the ordinary temperature to contain a given quantity of heat, like as a vessel contains a given quantity of water,

The heat of formation in aqueous solution can be calculated like that of the chloride or bromide, and is given by the expression



and, since the heat of solution is 14.9 Cal,¹ the heat of formation of the anhydrous iodide from lithium and iodine is expressed by



Lithium iodide resembles the chloride and bromide in the formation of double compounds with alcohols.² At 25° C, 250.8 grams of the salt dissolve in 100 grams of ethyl alcohol.³ With propyl alcohol it yields a complex of the formula



Like the other halides, lithium iodide forms double salts with other metallic iodides, such as those of mercury⁵ and lead.⁶

Lithium iodide tetrachloride,⁷ $LiICl_4 \cdot 4H_2O$, forms yellow, deliquescent needles, melting at 70° to 80° C, and is prepared by the action of chlorine and iodine on a saturated solution of lithium chloride in hydrochloric acid.

Lithium hypochlorite, $LiOCl$ — The hypochlorite is very unstable, and has not been isolated. It is formed in solution by the action of chlorine on a solution of lithium hydroxide,

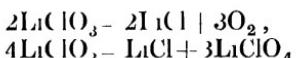


but is rapidly decomposed with formation of chlorate



It is probably also present in the product formed by the action of chlorine on dry lithium hydroxide.⁸

Lithium chlorate, $LiClO_3$ — On evaporation of the solution obtained by mixing aqueous solutions of lithium sulphate and barium chlorate, or by neutralizing chloric acid with lithium carbonate, lithium chlorate separates in needles. According to Potilitzin,⁹ the crystals thus obtained have the formula $2LiClO_3 \cdot H_2O$, but other investigators¹⁰ state that they consist of the anhydrous salt. Above 270° C the chlorate decomposes into chloride, perchlorate, and oxygen, in accordance with the equations



Lithium chlorate is more soluble in water than any other inorganic

¹ Bodislo *J Russ Phys Chem Soc* 1888, 20, 500, 1889, 21, 7

² Turner and Bissell *Trans Chem Soc* 1914, 105, 1777

³ Turner and Bissell *ibid* 1913, 103, 1904

⁴ Turner and Bissell *ibid* 1906

⁵ Dobrosserdy *J Russ Phys Chem Soc* 1901, 32, 774

⁶ Bogorodsky *ibid* 1893, 25, 316, 1894, 26, 209

⁷ Wells and Wheeler *Zeitsch anorg Chem* 1892, 2, 55

⁸ Kraut *Annalen* 1882, 214, 354; Junge and Naef *Ber*, 1883, 16, 840

⁹ Potilitzin *J Russ Phys Chem Soc* 1888, 20, 541

¹⁰ Mylius and Funk, *Ber*, 1897, 30, 1716; Rutgers *Zeitsch physikal Chem*, 1890,

ice and water. supposing the capacities of these two bodies to be as 9 to 10, at the temperature of 32° , it is known that ice of 32° requires as much heat as would raise water 150° , to convert it into water of 32° , or to melt it. Consequently, according to the 8th formula, page 57, water of 32° , must contain 10 times as much heat, or 1500° . That is, the zero must be placed at 1500° below the temperature of freezing water. Unfortunately, however, the capacity of ice has not been determined with sufficient accuracy, partly because of its being a solid of a bad conducting power, but principally because the degrees of the common thermometer below freezing, are very erroneous from the equal division of the scale.

Besides the one already mentioned, the principal subjects that have been used in this investigation are, 1st, mixtures of sulphuric acid and water, 2d, mixtures of lime and water, 3d, mixture or combination of nitric acid and lime, and 4th, combustion of hydrogen, phosphorus and charcoal. Upon these it will be necessary to enlarge.

Mixture of Sulphuric Acid and Water

According to the experiments of Lavoisier

temperatures¹ For the density of an impure specimen, Brauner and Watts² found at 15° C the value 2102 At a high temperature it attacks platinum,³ but its great stability is exemplified by its indifference towards hydrogen, carbon, and carbon monoxide

Lithium monoxide is slowly attacked by water, with formation of the intensely alkaline solution of the hydroxide The heat evolved is given by the equation⁴



Since the heat evolved by solution of 2 gram-atoms of lithium in water is 106.4 Cal (p 62), and the heat of formation of water is 68.3 Cal, the heat of formation of the oxide from its elements is given by the equation

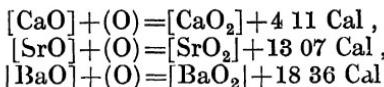


Lithium peroxide, Li₂O₂—Addition of alcohol to the aqueous solution obtained by the interaction of hydrogen peroxide and lithium hydroxide precipitates the crystalline product Li₂O₂, H₂O₂, 3H₂O, a substance converted by drying over phosphoric anhydride into the anhydrous peroxide, Li₂O₂. The method resembles that employed in the preparation of the peroxides of the alkaline-earth metals⁵ The combustion of lithium in oxygen yields only a small proportion of peroxide, a distinction from sodium The peroxide boils⁶ at 258° C

The heat of formation of the peroxide from the monoxide and oxygen is given by the equation⁶



the corresponding equations for the peroxides of calcium, strontium, and barium being



In this respect lithium displays close analogy to the alkaline earth-metals, occupying a position between calcium and strontium Further analogy is shown by the heat of formation of lithium peroxide from its elements,⁶



a value closely approximating to that of calcium peroxide,



Divergence from the other alkali metals is made evident by the fact that sodium peroxide has a considerably lower heat of formation⁷



Lithium hydroxide, LiOH—The hydroxide can be prepared from the

¹ Riecke and Endell *Sprechsaal* 1910, 43, 683

Brauner and Watts *Phil Mag* 1881 [5] 11, 60

² Riecke and Endell *loc cit*

³ de Forcrand *Compt rend*, 1907, 145, 702

⁴ de Forcrand, *ibid*, 1900, 130, 1465

⁵ de Forcrand *Ann Chim Phys* 1908, [8] 15, 433

⁶ de Forcrand, *Compt rend*, 1900, 130, 1465

proportions, observes the increase of temperature, and then finds the capacities of the mixtures. Whence we have data to find the zero by formula 9, page 58. In giving his numbers, I have changed his scale, the centigrade, to Fahrenheit's.

Acid	Water	heat evolv.	capa. of mix.	comp zero
4	+	1	194°	442
2	+	1	203	500
1	+	1	161	605
1	+	2	108	749
1	+	5	51	876
1	+	10	28	925
				1740

The mean of these is 2300°, which is far beyond what Gadolin supposes to be the zero, as deduced from the relative capacities of ice and water, and to which he seeks to accommodate these experiments

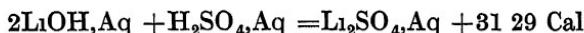
As the heat evolved upon the mixture of sulphuric acid and water is so considerable, and as all three articles are liquids, and consequently admit of having their capacities ascertained with greater precision, I have long been occasionally pursuing the investigation of the zero from experiments on these liquids. The strongest sulphuric acid of 1 855, I find has the specific heat 33, and

Lithium polysulphides —Fusion of lithium hydroxide with sulphur yields a yellow mass like "liver of sulphur," probably consisting of polysulphides of lithium. Berzelius isolated a hydrated disulphide, $\text{Li}_2\text{S}_2 \cdot n\text{H}_2\text{O}$, by concentrating an aqueous solution of the monosulphide.

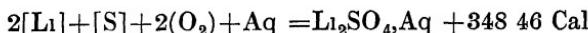
Lithium sulphite, Li_2SO_3 —Evaporation of the solution obtained by the action of sulphur dioxide on lithium carbonate suspended in water yields the monohydrate, $\text{Li}_2\text{SO}_3 \cdot \text{H}_2\text{O}$, addition of alcohol or ether precipitates the dihydrate, $\text{Li}_2\text{SO}_3 \cdot 2\text{H}_2\text{O}$. The sulphite is readily soluble in water, and is susceptible to atmospheric oxidation. Heat expels the water of crystallization, and causes partial decomposition into sulphate and sulphide. Double sulphites of lithium with potassium and sodium have been prepared¹.

Lithium sulphate, Li_2SO_4 —The hydrated sulphate, $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, is obtained in monoclinic plates² by evaporating a solution of sulphuric acid neutralized with lithium carbonate. Its density is 2.02 to 2.06. The anhydrous salt is said to have been prepared by Retgers,³ its melting-point being given by Huttner and Tammann⁴ as 859° C., by Ramsay and Eumorfopoulos⁵ as 853° C., and by Muller⁶ as 848° C. Its density is 2.21.

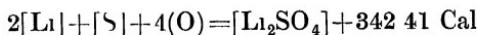
Lithium sulphate is readily soluble in water. The heat of formation in dilute aqueous solution from lithium hydroxide and sulphuric acid is given by the equation⁷



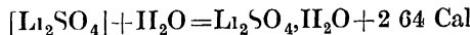
Since the heat evolved by solution of 2 gram-atoms of lithium in water is 106.4 Cal (p. 62), and the heat of formation of sulphuric acid from its elements⁸ is 192.92 Cal, and its heat of solution in water⁹ is 17.85 Cal, the heat of formation of the sulphate in dilute solution from the elements is given by the expression



Taking 6.05 Cal as the heat of solution of anhydrous lithium sulphate the value given by Thomsen,¹⁰ the equation for the heat of formation of the anhydrous sulphate becomes



For the heat of solution of the hydrate, $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, Thomsen¹⁰ gives the value 3.11 Cal, and for its heat of hydration¹¹ the equation is



References are appended to investigations on double sulphates

¹ Rohrig *J. prakt. Chem.* 1888 [2] 37 217

² Irzabe *Jahrb. Min.* 1892 n. 58

³ Retgers *Zeitsch. physikal. Chem.* 1891 8 33

⁴ Huttner und Tammann *Zeitsch. anorg. Chem.* 1905 43 224

⁵ Ramsay und Eumorfopoulos *Phil. Mag.* 1896 41 360

⁶ Muller *N. Jahrb. Mineral. Beil. Bd.* 1914 30 1 *Zeitsch. Kryst. Min.*, 1914 53 511

⁷ Thomsen, *Thermochemistry* (Longmans 1908) 115

⁸ Thomsen, *ibid.* 212

⁹ Thomsen, *ibid.* 47

¹⁰ Thomsen, *ibid.* 49

¹¹ Thomsen, *ibid.* 62

by weight, form four parts of hydrat, a perfectly dry powder, from which the water cannot be expelled under a red heat. If more water is added, the mixture forms mortar, a pasty compound, from which the excess of water may be expelled by a boiling heat, and the hydrat remains a dry powder. When hydrat of lime and water are mixed, no heat is evolved, hence the two form a mere mixture, and not a chemical compound. The heat then which is evolved in slaking lime, arises from the chemical union of three parts of lime and one of water, or from the formation of the hydrat, and any excess of water diminishes the sensible heat produced. Before any use can be made of these facts for determining the zero, it becomes necessary to determine the specific heat of dry hydrat of lime. For this purpose a given weight of lime is to be slaked with an excess of water, the excess must then be expelled by heat till the hydrat is $\frac{1}{3}$ heavier than the lime. A given weight of this powder may then be mixed with the same, or any other weight of water of another temperature, and its specific heat determined accordingly. By a variety of experiments made in this way, and with sundry variations, I find the specific heat of hydrat of

into needles, probably the anhydrous salt¹ and isomorphous with the corresponding sulphate and selenate. It yields a double salt with potassium, LiKCrO_4 . At 18° C , 100 grams of water dissolve 110.9 grams of the dihydrate².

A lithium dichromate has also been prepared³.

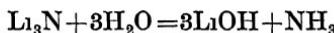
Lithium permanganate, LiMnO_4 .—The trihydrate, $\text{LiMnO}_4 \cdot 3\text{H}_2\text{O}$, forms dark-violet crystals, isomorphous with the perchlorate⁴. The manganate has not been isolated.

Lithium molybdates⁵.—By varying the experimental conditions, Ephraim and Brand⁶ have prepared six different molybdates by the interaction of lithium carbonate and molybdic acid. $\text{Li}_2\text{O} \cdot \text{MoO}_3$, $2\text{Li}_2\text{O} \cdot 3\text{MoO}_3$, $\text{Li}_2\text{O} \cdot 2\text{MoO}_3 \cdot 5\text{H}_2\text{O}$, $3\text{Li}_2\text{O} \cdot 7\text{MoO}_3 \cdot 28\text{H}_2\text{O}$, $\text{Li}_2\text{O} \cdot 3\text{MoO}_3 \cdot 7\text{H}_2\text{O}$, and $\text{Li}_2\text{O} \cdot 4\text{MoO}_3 \cdot 7\text{H}_2\text{O}$. They failed to obtain a salt with a higher proportion of MoO_3 .

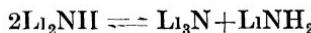
Ephraim and Brand have also described a number of phospho-molybdates of lithium⁷.

Lithium nitride, Li_3N .—The nitride is best prepared by the action of nitrogen on the metal at ordinary temperatures,⁸ the product being a grey, amorphous, hygroscopic substance, unaffected by dry hydrogen or air, but rapidly decomposed by moisture. It absorbs both nitrogen and oxygen from the air. A ruby red, crystalline modification is formed by the action of lithium on nitrogen at 450° to 460° C . It is less hygroscopic than the amorphous form, and does not absorb gases in the cold. At 840° to 845° C in a current of nitrogen the amorphous nitride becomes crystalline.

Water decomposes the nitride according to the equation



Guntz recommends the formation of the nitride as a convenient means of isolating argon,⁹ and its interaction with metallic chlorides as a method for preparing other nitrides¹⁰. For the heat of formation he found 49.5 Cal.¹¹ It is formed by the action of light on lithium imide, Li_2NII (p. 72).¹²



Lithium hydrazoate, LiN_3 .—Neutralization of hydrazoic acid with lithium hydroxide and concentration of the solution yields colourless needles of the monohydrate, $\text{LiN}_3 \cdot \text{H}_2\text{O}$. It is hygroscopic and explosive, and is decomposed by heat.¹³

Lithamide, LiNH_2 .—The amide can be prepared by the action of

¹ Retgers *Zeitsch physikal Chem* 1891 8 33

² Mylius und Fahl *ibid* 1897 30 1716

³ Rammelsberg *Pogg Annalen* 1866 128 311

⁴ Peters *Zeitsch physikal Chem* 1891 8 33

See also this series Vol VII Part III

⁶ Ephraim und Brand *Zeitsch anorg Chem* 1909 64 258

⁷ Ephraim und Brand *ibid* 1910 65 233

⁸ Dafert und Miklusz *Monatsh* 1910 31 981 compare Lenz *Ber Deut pharm Ges*, 1910 20 227 Guntz *Compt rend* 1895 121 946

⁹ Guntz *Compt rend* 1895 120 777

¹⁰ Guntz, *ibid* 1902 135 738

¹¹ Guntz *ibid* 1896 123 995

¹² Dafert and Miklusz *Monatsh*, 1912, 33 63

¹³ Dennis and Benedict *J Amer Chem Soc*, 1898, 20 225

of lime, is 619. But supposing there was no change of capacity upon combination, the compound should only have the capacity .618; whereas, in fact, the mixture produces an increase of temperature of about 180° , and therefore ought to be found with a diminished capacity, or one below .618. Were this fact to be established, it would exhibit an inexplicable phenomenon, unless to those who adopt the notion of *free* caloric and *combined* caloric existing in the same body, or to speak more properly, of caloric combined so as to retain all its characteristic properties, and caloric combined so as to lose the whole of them. One error in this statement has already been pointed out, in regard to the capacity of lime. If we adopt the specific heat of lime to be 30, and apply the theorem for the zero, we shall find it to be 15770° below the common temperature, as deduced from the above data so corrected.

I took a specimen of nitric acid of the specific gravity 1.2, and found, by repeated trials, its specific heat to be 76 by weight. Into 4600 grains of this acid of 35° temperature, in a thin flask, 657 grains of lime were gradually dropped, and the mixture moderately agitated; in one or two minutes after 3-4ths of the lime was in and dissolved, the thermometer

References to other investigations of the properties of dilute solutions of the nitrate are appended¹

The heat of formation of lithium nitrate in dilute solution is given by the equation



Its heat of solution is only 0.8 Cal, a phenomenon probably due to the

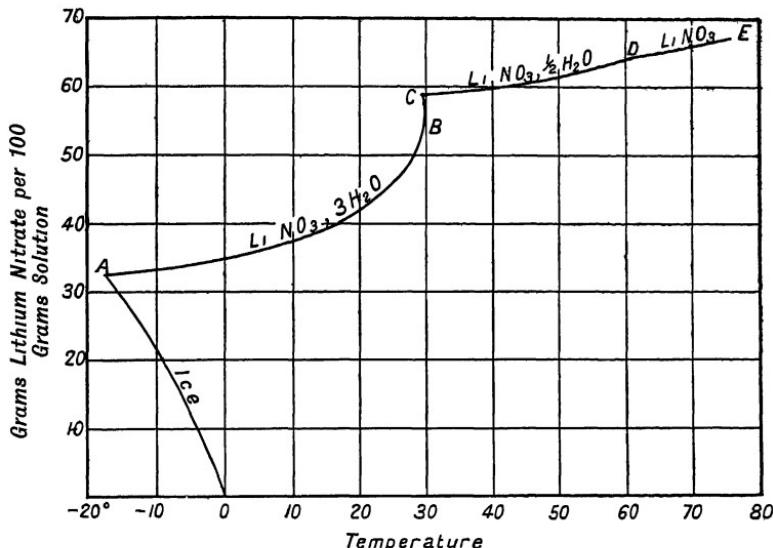
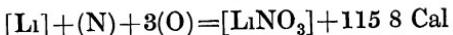


FIG. 4.—Solubility curve of lithium nitrate

formation of hydrates. It follows that the heat of formation of the anhydrous salt from its elements is given by



The heat of solution in alcohol is 4.66 Cal²

With ammonia in absence of water lithium nitrate forms a liquid characterized by its lack of action on machine steel, iron wire, or nichromic wire after contact for several months. It has been suggested that the addition of a small percentage of water would render the liquid a good absorbent for the removal of ammonia from mixtures of the gas with nitrogen and with hydrogen³.

The molecular electric conductivity of lithium nitrate between 272° and 440.6° C. is given by the formula⁴

$$\mu_t = 41.14 - 0.238(t - 300)$$

Lithium nitrate resembles the chloride in the non-formation of isomorphous mixed crystals with the corresponding sodium salt⁵.

¹ Jones and Getman, *Zeitsch physikal Chem* 1903, 46, 269; Jones and Lindsay, *Amer Chem J* 1902, 28, 329; Lincoln and Klein, *J Physical Chem* 1907, 11, 318; Hartley Thomas and Appleby, *Trans Chem Soc* 1908, 93, 538.

Pickering, *Trans Chem Soc* 1888, 53, 865.

² Davis, Olmstead and Lundstrum, *J Amer Chem Soc*, 1921, 43, 1575.

³ Jaeger and Kapma, *Zeitsch anorg Chem* 1920, 113, 27.

⁴ Krickmeyer, *Zeitsch physikal Chem*, 1896, 21, 85.

By adopting Crawford's capacities of hydrogen and oxygen, and applying the theorem, page 58, we find the zero 1290° from the common temperature. But if we adopt the preceding theory of the specific heat of elastic fluids, and apply the 4th corol page 72, we must conclude that in the formation of steam, one half of the whole heat of both its elements is given out, the conversion of 8lbs of steam into water, will give out heat sufficient to melt 56lbs of ice, therefore one half of the whole heat in 1lb of hydrogen, and 7lbs of oxygen together, or which is the same thing, the whole heat in 1lb of hydrogen, or 7lbs of oxygen separately, will melt 344lbs of ice, now if from 688 we take 400, there remain 288 for the lbs of ice, which the heat in 8lbs of water, at the ordinary temperature, is sufficient to melt, or the heat in 1lb is capable of melting 36lbs of ice hence the zero will be 5400° below freezing water.

Combustion of Phosphorus

One pound of phosphorus requires 1lb of oxygen, and melts 66lbs of ice. The specific heat of phosphorus is not known, but from analogy one may suppose it to have as much heat as oil, wax, tallow, &c which is nearly half as much as water. From the last article

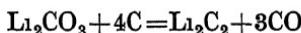
Lithium meta-arsenite, LiAsO_2 —At 25° C the ternary system *lithium oxide—arsenious oxide—water* indicates the existence of a meta-arsenite soluble in water without decomposition¹

Lithium arsenate, Li_3AsO_4 —The semihydrate, $2\text{Li}_3\text{AsO}_4 \cdot \text{H}_2\text{O}$, is obtained by the action of lithium carbonate on arsenic acid². The anhydrous salt is prepared by recrystallizing this hydrate from fused lithium chloride,³ its density at 15° C being 3.07. With excess of arsenic acid the normal salt yields deliquescent prisms of the *dihydrogen arsenate*, $2\text{LiH}_2\text{AsO}_4 \cdot 3\text{H}_2\text{O}$, from which water regenerates the trilithium salt⁴.

Lithium antimonide, Li_3Sb —Since the direct combination of lithium and antimony is very violent, Lebeau⁵ recommends preparing the antimonide by the electrolysis of a fused mixture of lithium and potassium chloride with an iron cathode covered with antimony. It is a dark-grey, crystalline substance of a very reactive nature. Its density at 17° C is 3.2, and its melting-point is 950° C . The compound is also formed by the action of antimony on a solution of lithium in liquefied ammonia.⁶

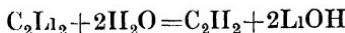
Lithium antimonate, $\text{LiSbO}_3 \cdot 3\text{H}_2\text{O}$ —The antimonate is precipitated in crystalline form on addition of potassium antimonate to a lithium salt in solution⁷. Like the sodium salt, it is only slightly soluble in water.

Lithium carbide, Li_2C_2 —The carbide was first prepared by Moissan⁸ by the reduction of lithium carbonate with charcoal in the electric furnace



Tucker and Moody⁹ were unable to prepare the almost pure carbide described by Moissan, and attributed their failure to the very small temperature interval between the formation and the decomposition of the substance. The carbide is also formed by the interaction of lithium and any of the allotropic modifications of carbon in vacuum at dull red heat, and by the combination of the metal with carbon monoxide or dioxide, or with ethylene or acetylene, an impure product is obtained¹⁰.

Lithium carbide is a white or grey crystalline substance, its density at 18° C being 1.65. At bright red heat it is decomposed, and Tucker and Moody found that at 925° C and a pressure of fifty pounds to the square inch it absorbs nitrogen slowly with formation of cyanamide, dicyanamide, and cyamide. It is a powerful reducer, decomposing water energetically at ordinary temperatures with formation of acetylene.



It ignites in fluorine and chlorine without the application of heat, and on gentle warming in the vapour of bromine, iodine, or phosphorus. It combines with oxygen, sulphur, and selenium at dull redness.

Guntz¹⁰ gives the heat evolved in its action on water as 371 Cal.

¹ Schreinemakers and de Bont *Rec. trav. chim.* 1920, 39, 423.

² Pannwitzberg *Pogg. Annalen*, 1866, 128, 311.

³ de Schulten *Bull. Soc. chim.* 1889, [3], 1, 479.

⁴ Pannwitzberg *loc. cit.*

⁵ Lebeau *Bull. Soc. chim.* 1902, [3], 27, 254.

⁶ Lebeau *ibid.* 256.

⁷ Balstein und von Blaese *Mélanges phys. et chim. de Bull. St. Petersbourg* 1889, 13, 1.

⁸ Moissan *Compt. rend.* 1896, 122, 362.

⁹ Tucker and Moody *J. Amer. Chem. Soc.*, 1911, 33, 1478.

¹⁰ Guntz *Compt. rend.*, 1896, 123, 1273; 1898, 126, 1866.

$$\frac{(1+26) \times 491 \times h}{1 \times 26 + 26 \times 1333 - 36 \times 491} = 6000^{\circ}$$

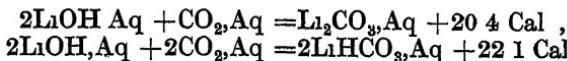
where h represents the degrees of temperature which the combustion of 1lb of charcoal would raise the product, or 36lbs of carbonic acid. From this, h is found = 6630°. But this heat would raise 36lbs. of water = $6650 \times 491 = 3265^{\circ}$. Or it would raise 1lb of water, 11750°, or it would melt 78lbs. of ice. Lavoisier finds the effect = 96lbs and Crawford finds it = 69. So that the supposed distance of the zero is not discountenanced by the combustion of charcoal, as far as the theory is concerned.

Combustion of Oil, Wax and Tallow

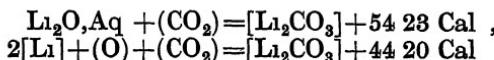
We do not know the exact costitution of these compounds, nor the quantity of oxygen which they require, but from the experiments of Lavoisier, as well as from some attempts of my own, I am inclined to think, that they are formed of about 5 parts of charcoal and 1 of hydrogen by weight, and that 6 parts require 21 of oxygen for their combustion, forming 19 parts of carbonic acid and 8 of water. Let it be supposed that the zero is 6900° below freezing water, or that the heat in water of 32°, is sufficient to melt 46lbs of ice, then

with charcoal yields the monoxide, sodium carbonate being reduced to the metal by similar treatment. At the temperature of the electric furnace excess of charcoal produces the carbide (p. 75), an example of the relationship between lithium and calcium.

The heat of formation of the normal carbonate and that of the primary carbonate have been calculated by Muller¹



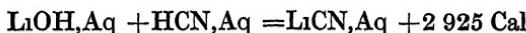
For the heat of formation of the solid normal carbonate de Forcrand² gives the equations



Basic carbonates have been described by Fluckiger,³ and a double salt with potassium by Le Chatelier.⁴

Lithium percarbonate, $\text{Li}_2\text{C}_2\text{O}_6$ —Electrolysis of a solution of lithium carbonate at -30° to -40° C yields a solution of the percarbonate, which liberates iodine from potassium iodide instantaneously. The crystalline salt has not been isolated.⁵

Lithium cyanide has not been isolated, but Varet⁶ has determined its heat of formation from the hydroxide and hydrocyanic acid



The low value is due to the heat absorbed during the ionization of the weak acid.

Lithium thiocyanate, LiCNS —The thiocyanate is obtained by neutralizing an aqueous solution of thiocyanic acid with lithium carbonate, and evaporating.⁷ It forms very deliquescent plates, readily soluble in alcohol.

Lithium silicide, Li_6Si_2 —By heating excess of lithium with silicon, and expelling the uncombined metal at 400° to 500° C, the silicide is obtained as a very hygroscopic, dark-violet, crystalline substance⁸ of density 1.12. It is a very reactive product and a powerful reducer. With concentrated hydrochloric acid it yields spontaneously inflammable silicoethane, Si_2H_6 , of which it may be considered a derivative.

Lithium silicates—Fusion of sand with lithium chloride yields the *orthosilicate*, Li_4SiO_4 , the *metasilicate*, Li_2SiO_3 , and an *acid silicate*, $\text{Li}_2\text{O}, 5\text{SiO}_2$.⁹ When the chloride is replaced by the carbonate, the same substances are formed,¹⁰ also another *acid silicate*,¹⁰ $\text{Li}_2\text{O}, 2\text{SiO}_2$, and a *subsilicate*, Li_8SiO_6 .¹¹ A study by Niggli¹¹ has proved the system

¹ Muller *Ann. Chim. Phys.* 1888, [6] 15 517

² de Forcrand *Compt. rend.* 1908, 146, 511

³ Fluckiger *Arch. Pharm.*, 1887, [3] 25 509

⁴ Le Chatelier *Ztsch. physikal. Chem.* 1896, 21 557

⁵ Riesenfeld and Reinhold *Ber.*, 1909, 42 4377

⁶ Varet *Compt. rend.* 1895, 121 598

⁷ Hermes *J. prakt. Chem.* 1866, 97 465

⁸ Moissan *Compt. rend.*, 1902, 134, 1083 135 1284

⁹ Hautefeuille and Margottet, *ibid.* 1881, 93 686

¹⁰ Rieke and Endell, *Sprechsaal*, 1912, 44 97

¹¹ Niggli, *J. Amer. Chem. Soc.*, 1913, 35, 1693

the difference may well be attributed to the loss unavoidable in my method of observation

I might here enquire into the results of the combustion of the other articles mentioned in the table, page 78, as far as they affect the present question; but I consider those above noticed as the most to be depended upon. From the result of olefiant gas we may learn that a combustible body in the gaseous state does not give out much more heat than when in a liquid state, for, oil and olefiant gas certainly do not differ much in their constitution; one would therefore have expected the same weight of olefiant gas to have yielded more heat than oil, because of the heat required to maintain the elastic state, but it should seem that the heat requisite to convert a liquid into an elastic fluid, is but a small portion of the whole, a conclusion evidently countenanced by the experiments and observations contained in the preceding pages.

It may be proper now to draw up the results of my experience, reported in the present section, into one point of view.

Lithium borates—A borate of the formula $\text{LiBO}_2 \cdot 8\text{H}_2\text{O}$ crystallizes from mixed solutions of lithium hydroxide and boric acid. At 47° C it melts in its water of crystallization, loses seven molecules of water at 110° C , and the eighth at 160° C . The tenacity with which the final molecule of water is retained points to the possibility of the salt being an orthoborate, $\text{LiH}_2\text{BO}_3 \cdot 7\text{H}_2\text{O}$.¹ At 147° C its density is 1.397.

The anhydrous metaborate, LiBO_2 , is precipitated by the interaction of alcoholic solutions of a lithium salt and boric acid,² and can also be obtained by fusing lithium carbonate with boric acid.³ It forms trichinic leaflets of pearl-like lustre, and melts⁴ at 843° C . Boiling with water converts it into the octahydrate.

Le Chatelier's data for the solubility of the anhydrous metaborate in water are given in the following table.⁵

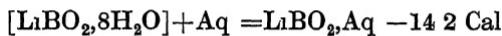
Solubility of Lithium Metaborate

Temperature, °C	0	10	20	30	40	45
Grams LiBO_2 in 100 grams of water	0.7	1.4	2.6	4.9	11	20

For the heat of hydration Le Chatelier found



and for the heat absorbed by solution of the hydrate



A polyborate, $\text{Li}_2\text{B}_8\text{O}_{13}$, is obtained in crystalline form by heating lithium carbonate with excess of boric acid at 500° to 600° C for a long time.⁶

DETECTION AND ESTIMATION OF LITHIUM

The flame coloration and the spectrum (p. 54) afford delicate tests for the presence of lithium. From solutions which are not too dilute it can be precipitated as phosphate, fluoride, or carbonate. Like sodium, it yields an antimonate of slight solubility, but in contradistinction to potassium its platino chloride and hydrogen tartrate are soluble.

The quantitative estimation of lithium can be effected by conversion into the sulphate or chloride. When other alkali-metals are present, Treadwell⁷ recommends Gooch's⁸ method, which involves conversion into chloride, separation of this salt by solution in amyl alcohol, and transformation into lithium sulphate. A modification of Gooch's method, devised by Rammelsberg and modified by Treadwell,⁹ involves the extraction of the lithium chloride with a mixture of equal

¹ Reischle *Ztsch anorg Chem* 1893, 4, 169, compare Rosenheim and Reglin *ibid* 1921, 120, 103;

Reischle *loc cit*

² Le Chatelier *Compt rend* 1897, 124, 1091; *Bull Soc chim* 1897, [3], 17, 585

³ van Klooster *Ztsch anorg Chem* 1910, 69, 122

⁴ Le Chatelier *Compt rend* 1897, 124, 1091

⁵ Le Chatelier *Bull Soc chim* 1899, [3], 21, 34

⁶ Treadwell *Analytical Chemistry*, 1st ed. (Wiley, 1904), 2, 51

⁷ Gooch *Chem News* 1887, 55, 18, 29, 40, 56, 78

⁸ Treadwell *Analytical Chemistry*, 1st ed. (Wiley, 1904), 2, 52

the same cause, namely, from a condensation of volume, and consequent diminution of capacity of the excited body, exactly in the same manner as the condensation of air produces heat. It is a well known fact, that iron and other metals, by being hammered, become hot and condensed in volume at the same time, and if a diminution of capacity has not been observed it is because it is small, and has not been investigated with sufficient accuracy. That a change of capacity actually takes place cannot be doubted, when it is considered, that a piece of iron once hammered in this way, is unfitted for a repetition of the effect, till it has been heated in a fire and cooled gradually. Count Rumford has furnished us with some important facts on the production of heat by friction. He found that in boring a cannon for 30 minutes, the temperature was raised 70° , and that it suffered a loss of 837 grains by the dust, and scales torn off, which amounted to $\frac{1}{47}$ part of the cylinder. *On the supposition that all the heat was given out by these scales*, he finds they must have lost 66360° of temperature, when at the same time he found their specific heat not sensibly diminished. But this is manifestly an incorrect view of the subject the heat excited does not arise from the scales merely, else how

CHAPTER IV

SODIUM

Symbol, Na Atomic weight, 23.00 (O=16)

Occurrence—Although sodium in the free state is not found in nature, it is present in combination in most minerals. *Soda-felspar* or *albite* is a double silicate of sodium and aluminium, $3\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 6\text{SiO}_2$. Seawater contains 2.6 to 2.9 per cent of sodium chloride, NaCl , the deposits left by the evaporation of inland seas being known as *rock-salt*. Both the carbonates and the sulphate of sodium occur dissolved in the water of many mineral springs, while the sulphate is a constituent of certain double salts, such as *glauberite* or sodium calcium sulphate, and *blodite* or sodium magnesium sulphate. Great deposits of *Chile saltpetre* or sodium nitrate, NaNO_3 , are present in Chile. *Cryolite* or sodium aluminium fluoride, $3\text{NaF}, \text{AlF}_3$, is an important mineral found in Greenland. Sodium carbonate occurs in South America and Egypt, and is also found as *gaylussite*, a double carbonate of sodium and calcium. *Tincal* or disodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7, 10\text{H}_2\text{O}$, is native to Thibet, India, and California, and a double borate of sodium and calcium called *cryptomorphite* is also found.

History—The knowledge of sodium carbonate or "soda" is of great antiquity, as indicated by two references in the Bible¹. The word translated "nitre" in the Authorized Version means "natron" or "soda," and is correctly rendered "lye" in Jer ii 22 in the Revised Version. No alteration has been made in the other reference. The confusion of terms evidently originated in the resemblance between the Greek *νιτρον* employed by Dioscorides and the Latin *nitrum* used by Pliny to denote sodium carbonate, and the word "nitre," loosely employed in early English as synonymous with "natron" or "soda," but now reserved for potassium nitrate.

In the sixteenth century Biringuccio seems to have appreciated the distinction between "nitrum" or soda and "sal nitrī" or saltpetre. Somewhat earlier the Arabs introduced into Europe the words "natrun," "natrum," and "natron," signifying soda, and "nitrum," meaning saltpetre. They also introduced the word "alkali" (p. 1), but drew no distinction between soda, derived from the ashes of sea plants, and potash, obtained from the ashes of land plants. These substances were denominated "fixed alkali" in contradistinction to the volatile ammonium carbonate.

In 1786 Duhamel de Monceau noted the difference between the "mineral alkali" or soda obtained from rock salt and the "vegetable

¹ Jeremiah ii 22 Proverbs xxv 20

of the motion of heat in the same body, and in its passage from one body to another, arising from its incessant tendency to an equilibrium

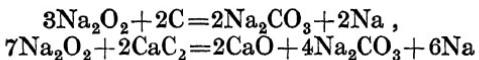
A solid bar being heated at one end, and exposed to the air, the heat is partly dissipated in the air, and partly conducted along the bar, exhibiting a gradation of temperature from the hot to the cold end. This power of conducting heat varies greatly, according to the nature of the subject in general, metals, and those bodies which are good conductors of electricity, are likewise good conductors of heat, and *vice versa*

When a fluid is heated at its surface, the heat gradually and slowly descends in the same manner as along a solid, and fluids seem to have a difference in their conducting power analogous to that of solids. But when the heat is applied to the bottom of a vessel containing a fluid, the case is very different. The heated particles of the fluid, in consequence of their diminished specific gravity form an ascending current and rise to the surface, communicating a portion of heat in their ascent to the contiguous particles, but still retaining a superiority of temperature, so that the increase of temperature in the mass is first observed at the surface, and is constantly

lower part is surrounded by a seal of solid sodium hydroxide (*H*) The positive electrode (+*E*) encircles the upper part of the negative electrode, but is separated from it by a diaphragm consisting of a cylinder of wire-gauze (*D*) attached to the bottom of the chamber (*C*) Being specifically lighter than the electrolyte, the liberated sodium (*S*) rises to the surface It is directed by the diaphragm (*D*) into the tubular iron chamber (*C*) placed over the negative electrode (-*E*), and is collected by means of ladles perforated to allow the molten hydroxide to drain off The gas liberated escapes at the opening (*O*) The periodic addition of fresh sodium hydroxide enables the process to be carried on continuously A current of 1000–1200 ampères at 4–5 volts is employed, and serves to maintain the temperature after fusion is complete The yield of sodium is between 40 and 50 per cent of the theoretical amount

In another electrolytic method formerly worked commercially, fused sodium chloride¹ was employed as electrolyte There are several practical difficulties to be overcome in carrying on this process, due partly to the corrosive nature of the chlorine liberated, and partly to the tendency to form the so-called subchloride of sodium Either the formation of this subchloride must be prevented, or, if produced, it must not be permitted to regenerate sodium chloride by interaction with the chlorine evolved at the anode The chlorine can be removed by contact at the anode with a heavy metal, such as lead, copper, or silver² Lowering the temperature of fusion by admixture with chloride of potassium or of an alkaline-earth metal,³ or with sodium fluoride,⁴ prevents the formation of the subchloride

Electrolytic processes are gradually displacing the older chemical methods of isolating sodium dependent on the reduction of the carbonate or hydroxide with charcoal or iron⁵ On a small scale, magnesium can be employed as reducer⁶ A laboratory method is the reduction of the peroxide with wood charcoal, coke, graphite, or calcium carbide⁷



Hydrogen is a usual impurity in metallic sodium, and is evolved when the metal reacts with mercury⁸ It can be removed by prolonged heating in vacuum⁹

Physical Properties—Sodium is a silver-white metal, rapidly tarnished by atmospheric oxidation, the process being attended by a greenish phosphorescence¹⁰ In thin layers by transmitted light the

¹ Fischer *Zeitsch Elektrochem* 1901 7 349

² Hopner *German Patent* 1884 No 30414 Ashcroft *ibid* 1903 No 158574

³ Grabau *ibid*, 1890 No 56230

⁴ Konsort für elektrochem Indust Nuernberg *ibid* 1904 No 160540 compare Darling *ibid* 1902 No 83097 *J Franklin Inst* 1902 153 65

⁵ Graham Otto *Lehrbuch der Chem*, 3rd ed, Brunswick 1885 1 281, Schadler, *Analen* 1836 20 2 Deville *Ann Chem Phys* 1856 [3] 46 415 Donny und Muesca *Graham Otto's Lehrbuch der Chem*, 3rd ed, Brunswick 1885 1 1 56 Wulcan *Chem News* 1891 64 239 Chem Fabrik Griesheim Fikction *German Patent* 1901 No 133665 Deville *Ann Chem Phys* 1855 [3] 43 5 Castner *German Patent* 1886 No 40415 Thomas *British Patent* 1884, No 6367 Thompson *ibid* 1879 No 2101

⁶ Winkler, *Ber* 1890 23 46 ⁷ Bambeiger, *Ber* 1898 31 54

⁸ Kahlenberg and Schlundt, *J Physical Chem*, 1905, 9, 257

⁹ Salet, *Ber*, 1876, 9 354

¹⁰ Linnemann, *J prakt Chem*, 1858, 75, 128 On the preparation and preservation of untarnished specimens, compare Bornemann, *Zeitsch angew Chem*, 1922 35, 227

heat, and the heat, so propelled, is called *radiant heat*

Till lately we have been used to consider the light and heat of the sun as the same thing. But Dr Herschel has shewn, that there are rays of heat proceeding from the sun, which are separable by a prism from the rays of light, they are subject to reflection, like light, and to refraction, but in a less degree, which is the cause of their separability from light. The velocity of radiant heat is not known, but it may be presumed to be the same as that of light, till something appears to the contrary. An ordinary fire, red hot charcoal, or indeed any heated body, radiates heat, which is capable of being reflected to a focus, like the light and heat of the sun, but it should seem to be not of sufficient energy to penetrate glass, or other transparent bodies so as to be refracted to an efficient focus.

Several new and important facts relative to the radiation of heat, have lately been ascertained by Professor Leslie, and published in his "Enquiry on Heat." Having invented an ingenious and delicate air thermometer, well adapted for the purpose, he was enabled to make the effects of radiation in a great variety of cases and circumstances, with more precision than had previously been done. Some

to the interaction of the vapour and the platinum, silver, iron, porcelain, or glass of the containing vessel.

The molecular weight was determined by Kraus¹ to be 28 by dissolving the metal in liquid ammonia, other investigators² give values for the molecular formula varying between $\text{Na}_{0.5}$ and Na_6 .

The value of the specific heat at 0° C is given by Griffiths³ as 0.2829. The specific heat from -185° to 20° C is 0.2845, according to Nordmeyer and Bernoulli⁴, from -84° to 7° C Regnault⁵ gives 0.2943, from -79.5° to 17° C Schuz⁶ gives 0.2830, and from 0° to 157° C Bernini⁷ gives values varying between 0.2970 and 0.333. For the specific heat of the solid at the melting-point, Rengade⁸ gives 0.3266. According to Itatka,⁹ the specific heat of the solid is 0.330, and of the liquid 0.347, the corresponding values for the atomic heat being 7.59 and 7.98.

The latent heat of fusion per gram is, according to Joannis,¹⁰ 31.7 cal, but Bernini¹¹ gives 17.75 cal, and Rengade¹² 27.23 cal.

Sodium is a good conductor of heat, and as a conductor of electricity it stands next to silver, copper, and gold. Its electric conductivity has been studied by several investigators¹³.

The mean value¹⁴ of the density is 0.978. Gay-Lussac and Thenard¹⁵ give the density at 15° C as 0.972 (water at 15° C = 1), Hackspill¹⁶ gives 0.9723 at 0° C, Schroder¹⁷ 0.985 compared with water at 3.9° C, Braumhauer¹⁸ 0.9785 at 13.5° C and 0.9748 at 10° C compared with water at the same temperatures, Vicentini and Omodei¹⁹ give 0.9519 for the solid at the melting point and 0.9287 for the liquid, Ramsay²⁰ 0.7414 for the liquid at the boiling-point, Dewar²¹ 0.9724 at 0° C and 1.0066 at the temperature of liquid air (water at 0° C = 1), and Richards and Brink²² 0.9712 at 20° C.

The value last mentioned for the density gives 28.70 as the atomic

¹ Kraus *J Amer Chem Soc* 1908 30 1197

² Ramsay, *Trans Chem Soc*, 1889 55 521 Meyer *Zeitsch physikal Chem* 1891, 7, 477 Haber and Sack *Zeitsch Elektrochem* 1902 8 245 Haber *Zeitsch physikal Chem* 1902 41 399 Tammann *ibid* 1889 3 441 Heycock and Neville *Trans Chem Soc* 1889 55 666 1890 57 376 1892 61 904 *Phil Trans* 1897 189 [A] 25 Abegg and Sackur *Winkelmann's Handbuch der Physik* 2nd ed, Leipzig 1906 3 797

³ Griffiths *Proc Roy Soc* 1914 [A] 89 561

⁴ Nordmeyer and Bernoulli *Ber deut physikal Ges* 1907 5 175 compare Nord *meier ibid* 1908 6 202

⁵ Regnault *Pogg Annalen* 1856 98 396

⁶ Schuz *Wied Annalen* 1892 46 177

⁷ Bernini *Physikal Zeitsch* 1906 7 168

⁸ Pechhold *Bull Soc chim* 1914 [4] 15 130

⁹ Itatka *Rep Iôhoku Imp Univ* 1910 8 99

¹⁰ Joannis *Ann Chim Phys* 1887 [6] 12 381

¹¹ Bernini *Physikal Zeitsch* 1906 7 168

¹² Rengade *Bull Soc chim* 1914 [4] 15 130

¹³ Matthiessen *Pogg Annalen* 1857 100 177 Bernini *Cimento* 1904 [5] 8 262 *Physikal Zeitsch* 1904 5 241 Guntz and Biernowksi *Compt rend* 1908 147 1474 Muller *Metallurgie* 1910 730 755 Hackspill *Compt rend* 1910 151 305

¹⁴ Iandolt-Bornstein and Myslinski *Tabellen* 3rd ed Berlin 1905 226

¹⁵ Gay-Lussac and Thenard *Gmelin Kaut and Friedheim's Handbuch der anorg Chem* 7th ed Heidelberg 1910 2 277

¹⁶ Hackspill *Compt rend* 1911 152 259 *Ann Chim Phys* 1913 [8] 28 613

¹⁷ Schroder *Pogg Annalen* 1859 106 226 107 113

¹⁸ Braumhauer *Ber* 1873 6 655

¹⁹ Vicentini and Omodei *Wied Annalen*, Beibl., 1888, 12 176

²⁰ Ramsay *Ber* 1880 13 2145

²¹ Dewar *Chem News* 1902 85 289

²² Richards and Brink *J Amer Chem Soc*, 1907, 29 117

absorb it in any remarkable degree , whereas black paint, paper, glass, &c. are disposed to absorb it, and consequently to radiate it again in proper circumstances

4 Screens of glass, paper, tinfoil, &c being placed between the radiating body and the reflector, were proved to intercept the radiant heat completely , but being heated themselves by the direct radiant heat, in time the thermometer was affected by their radiation The heat radiating from hot water, does not then seem capable of being transmitted through glass, like the solar heat

5 Radiant heat suffers no sensible loss in passage through the air , a greater or less radiant body produces the same effect, provided it subtends the same angle at the reflector, agreeing with light in this respect

6 The intensity of reflected heat diminishes inversely as the distance , whereas, in light it is the same at all distances , the focused heat too differs from that of light , it is near the reflector, the heating effect diminishes rapidly in going outwards, but slowly increasing inwards towards the reflector — This seems to intimate the want of perfect elasticity in radiant heat

7 A hollow globe of tin, four inches diameter, being filled with hot water, coo

at 18° C is 43.4, and at 25° C is 51.2. References to investigations of other properties of this ion are appended.¹

Transmutation of Copper into Sodium—In their account of their researches on the action of the radium emanation on solutions of copper salts, Cameron and Ramsay² state that sodium is probably a product of the action of the emanation on a solution of copper sulphate.³

Applications—Sodium is employed in the manufacture of sodium peroxide, sodamide, and sodium cyanide, and also in organic syntheses. In the laboratory it finds application in the preparation of pure sodium hydroxide, and in presence of alcohols as a reducer.

Atomic Weight—There is a very close association between the atomic weight of sodium and the atomic weights of potassium, silver, chlorine, bromine, and iodine, each element having been an important factor in the experimental investigation of both its own atomic weight and the atomic weights of the other five. The method of determining the ratio of the atomic weights of these elements to that of oxygen was originated by Berzelius, and was developed by Marignac and Stas. It involves three stages.

(1) The determination of the molecular weights of the chlorides, bromides, and iodides of sodium, potassium, and silver by analysis of the salts RXO_3 ($\text{R}=\text{metal}$, $\text{X}=\text{halogen}$), and induction from the ratios RX/SO_3 .

(2) The determination of the three ratios Ag/NaX , of the three Ag/KX , and of the three Ag/AgX , values for the atomic weight of silver being obtained from these ratios in conjunction with the previously determined molecular weights of the metallic halides NaX , KX , and AgX .

$$\frac{\text{RX}}{\text{SO}_3} \times \frac{\text{Ag}}{\text{RX}} = \frac{\text{Ag}}{\text{SO}_3}$$

(3) The determination of the six ratios AgX/RX , and the calculation of additional values for the atomic weight of silver from the expression

$$\frac{\text{RX}}{\text{SO}_3} \times \frac{\text{AgX}}{\text{RX}} \times \frac{\text{Ag}}{\text{AgX}} = \frac{\text{Ag}}{\text{SO}_3}$$

From the results obtained in (2) and (3) for the atomic weight of silver, a mean value is derived. Employing this figure, the molecular weights of the silver halides are calculated from the ratios Ag/AgX , compared with those obtained directly in (1), and mean values derived. Subtraction of the atomic weight of silver from these mean values gives the atomic weights of the halogens. Having thus ascertained the atomic weights of silver and the halogens, the molecular weights of the alkali metal halides are calculated from the ratios Ag/RX , and also

¹ Wilsdorf *Zeitsch physikal Chem* 1900 35 291 Haber and Sack *Zeitsch Elektrochem* 1902 8 246 Ostwald *Zeitsch physikal Chem* 1888 2 36 270 Rudolph *ibid* 1895 17 385 von Hoff *ibid* 1895 18 300 Storch *ibid* 1895 19 13 Kohlrausch *ibid* 1895 18 662 Roloff *Zeitsch angew Chem* 1902 15 525 561 585 Jahn *Zeitsch physikal Chem* 1900 35 1 Biltz *ibid* 1902 40 185 Abegg and Bodlander *Zeitsch anorg Chem* 1899 20 496 Kahlenberg *J Physical Chem* 1901 5 375 Drucker *Zeitsch Elektrochem* 1907 13 81, compare Abegg *Theorie der electrolyt Dissoziation* Stuttgart 1903 81 and Drucker *Anomalie der starken Elektrolyte*, Stuttgart 1905

Cameron and Ramsay *Trans Chem Soc*, 1907 91, 1593

² See p 55

fractional parts of its excess of temperature, by the three distinct sources of refrigeration in the air undermentioned :

By abduction, that is, the proper conducting power of air, the 524^{th} .

By recession, that is, the perpendicular current of air excited by the heated body, the $h \times 21715^{\text{th}}$

By pulsation, or radiation, the 2533^{d} part from a metallic surface, and eight times as much, or the 317^{th} part from a surface of paper, (It should be observed, that Mr Leslie contends that air is instrumental in the radiation of heat, which is contrary to the received opinion)

11 A body cools more slowly in rarefied air, than in air of the common density and the different species of air have their respective refrigerating powers Common air and hydrogenous gas exhibit remarkable differences According to Mr Leslie, if the cooling power of common air upon a vitreous surface be denoted by unity, that of hydrogenous gas will be denoted by $2,2857$, and upon a metallic surface the ratio is 5 to 1 7857 In common air the loss from a vitreous surface is 57 by radiation, and 43 by the other two causes from a metallic surface, 07 and 43 In hydrogenous gas the loss from a vitreous surface is 57

SODIUM.

89

The earlier determinations of the ratios involving the atomic weight of sodium commence with the work of Penny¹ in 1839. Four analyses of sodium chlorate gave as the mean result

$$\text{NaClO}_3 \cdot 3\text{O} = 100 \pm 0.0705 \pm 0.0029$$

Several early series of analyses of sodium chloride are available in which the silver necessary to combine with the chlorine in a known weight of sodium chloride was determined. The results of these experiments are given in the table

Experimenter	Date	$\text{Ag NaCl} = 100 x$, where $x =$
Pelouse ²	1845	54.141 ± 0.0063
Dumas ³	1859	54.172 ± 0.0096
Stas ⁴	1860	54.2078 ± 0.0002
Stas ⁵	1876-1882	54.2047 ± 0.00045

In Stas's second research allowance was made for the solubility of silver chloride in water, and for the presence of a trace of silica in the salt. Clarke has calculated the weighted mean of these four series of experiments to be

$$\text{Ag NaCl} = 100 \quad 54.2071 \pm 0.00018$$

The corresponding ratio for sodium bromide was also determined by Stas⁶ to be

$$\text{Ag NaBr} = 100 \quad 95.4405$$

Two series of determinations of the ratio

$$\text{AgCl NaCl} = 100 \quad x$$

should be mentioned. The first was carried out by Berzelius⁷ in 1811, and gave $x=40.885$, the second was made incidentally by Ramsay and Miss Aston⁸ in their work on the atomic weight of boron, and gave $x=40.867$. Both these results are much too high.

The values obtained by Stas for the atomic weights of silver, chlorine, and bromine were 107.930, 35.457, and 79.952, and were employed for many years⁹. By their aid the atomic weight of sodium can be calculated from the results already cited. From Penny's experiments ($\text{NaClO}_3 \cdot 3\text{O}$) it follows that $\text{NaCl} = 58.500$. From the mean ratio Ag NaCl it can be calculated that $\text{NaCl} = 58.506$. The average result is $\text{NaCl} = 58.503$. From the ratio Ag NaBr it follows that $\text{NaBr} =$

¹ Penny *Phil Trans* 1839 129 25

Pelouse *Compt rend* 1845 20 1047

² Dumas *Ann Chém Phys* 1859 [3] 55 182

³ Stas *Oeuvres Complètes* Brussels, 1894, I 370

⁴ Stas *ibid* 768 778

⁵ Stas *ibid*, 796

⁷ Berzelius *Afhandlingar i Fysik Kemi, etc* Stockholm 1806-1816 5 117
Gilbert's *Annalen* 1811 38 171

⁸ Ramsay and Miss Emily Aston *Trans Chem Soc* 1893 63 211

⁹ A mathematical computation from all the early data leads to approximately the same values

Correspondences of the Thermometric Scales

old scale	new scale	old scale	new scale,
212°	212°	409° 8	342°
225	222	427 3	352
238 6	232	445 3	362
252 6	242	463 6	372
266 8	252	482 2	382
281 2	262	501	392
296 2	272	520 3	402
311 5	282	539 7	412
327	292	559 8	422
342 7	302	580 1	432
359 2	312	600 7	442
375 8	322	621 6	452
392 7	332	642	762

Experiment 1

A mercurial thermometer having a bulb of half an inch in diameter, and a scale of about 8 inches long from freezing to boiling mercury, was heated to 41° new scale, and suffered to cool in a horizontal position in air of 12°. The bulb in this and every other instrument projected several inches below the scale. The times of cooling were the same from 142° to 212°, from 212° to 112°, and from 142° to 92°, namely, 2 minutes and 20 seconds each. This was often repeated, the times of cooling were always within 4 or 5 seconds of that above, and when any differences in the

11 experiments Cl NaCl=100 : 164.858, whence Na=22.997
 8 experiments Br NaBr=100 : 128.776, whence Na=22.997.

In the work of Richards and Hoover¹ in 1915, pure sodium carbonate was exactly neutralized with a solution of hydrobromic acid standardized against pure silver. They found that



Hence, if Ag=107.880, the molecular weight of sodium carbonate is 105.995, so that $2\text{Na} + \text{C} = 57.995$. A review of the atomic weight of carbon² indicates that the value is probably between 12.000 and 12.005. It follows that the atomic weight of sodium must lie between Na=22.995 and Na=22.998.

The modern work of Richards and Wells, Goldbaum, and Richards and Hoover indicates a value between 22.995 and 22.998 for the atomic weight of sodium. In the account of his work in 1915, Richards gave the preference to the lower number. In this series of text-books, the value Na=22.996 has been adopted for the computation of other atomic weights. The current table of the International Committee on Atomic Weights gives

$$\text{Na}=23.00$$

COMPOUNDS OF SODIUM³

Sodium hydride, NaH—By heating sodium contained in an iron vessel inside a sealed glass tube in an atmosphere of hydrogen, Moissan⁴ obtained sodium hydride in white crystals which condensed on the cooler part of the glass tube. The temperature of reaction is about 360° C, and is a factor of importance, since for sodium hydride the interval between the temperature of formation and that of decomposition is small. Much larger quantities of the hydride can be prepared⁵ by passing a rapid current of hydrogen over the surface of sodium heated to such a temperature above 350° C as produces a yellow glow. The hydride is carried off as a white smoke, and after electrical precipitation is filtered through glass-wool. The presence of metallic calcium facilitates its formation.

The density of the hydride is 0.92,⁶ and the vapour tension for each interval of 10° between 300° C and 410° C is 15, 17, 21, 27, 38, 55, 87, 136, 201, 285, 396, and 540 mm respectively.⁷ Sodium hydride is the most stable of the alkali metal hydrides, and cesium hydride the least. The sodium derivative is unaffected by dry air, but decomposes in presence of traces of moisture. Although insoluble in organic solvents such as carbon disulphide, carbon tetrachloride, benzene, and turpentine, it dissolves in the alkali metals and their amalgams.

¹ Richards and Hoover *J. Amer. Chem. Soc.* 1915, 37, 95.
 This series Vol V, 64.

² For sodium amalgam see this series Vol III. Alloys with potassium are mentioned on p. 159.

⁴ Moissan *Compt. rend.* 1902, 134, 71; compare Flster and Geitel *Physikal. Zeitsch.*, 1910, II, 257.

⁵ Fphram and Michel *Helv. Chim. Acta* 1921, 4, 762.

⁶ Moissan *Compt. rend.* 1902, 134, 71.

⁷ Fphram and Michel *Helv. Chim. Acta*, 1921, 4, 762, compare Keyes *J. Amer. Chem. Soc.*, 1912, 34, 779.

with tinfoil, pasted upon it, and the surface made as smooth as well could be, the thermometer was then heated, and the times of cooling were again noticed as before, repeatedly. The mean results follow; and a column of the differences of the logarithms of the degrees expressing the elevation of temperature above that of the surrounding air, which was 40° . The temperature of the thermometer was raised to 275° per scale, that is, 235° above the air, and it is obviously most convenient to reckon from the temperature of the air considered as zero in which case 19 represents the difference of the logarithms of 235 and 225, &c.

Thermom. cooled		Bull clear seconds	Bulb cov with tinfoil seconds	Dif of Logarith
From 235°	to 225°	19	17	19
225	to 215	12	18	20
215	to 20,	13	14	21
20,	to 19,	14	13	22
19,	to 18,	15	21	23
18,	to 17,	16	22	24
175	to 165	17	24	25
165	to 155	19	21	27
155	to 145	20	21	29
145	to 135	21	23	31
135	to 125	22	21	33
125	to 115	24	18	36
115	to 105	27	16	39
105	to 95	40	40	43
95	to 85	31	48	48
85	to 75	39	54	54
75	to 65	45	62	62
65	to 55	64	73	73
55	to 45	62	88	87
45	to 35	78	110	109
35	to 25	120	165	146
25	to 15	160	244	222

15° C and -52° C . The freezing point of NaCl is -26.7° C , and the boiling point of the aqueous solution is 106.3° C .

Sodium hydrochloride. $\text{NaCl} \cdot \text{H}_2\text{O}$ — A crystalline compound which is obtained by the action of hydrochloric acid on sodium hydroxide. It decomposes when heated to a temperature of 162° C . It is soluble in water, but more slowly than at 20° C . The heat of solution is given by Guntz³ as -16.2 Cal , and the heat of formation from solid sodium chloride and gaseous hydrochloric acid as 17.1 Cal .

Sodium chloride. NaCl — Large quantities of sodium chloride are found in nature, the average amount present in the water of the ocean being about 27 per cent, while certain inland lakes contain a much higher percentage. The Great Salt Lake in Utah has up to 30 per cent of the chloride in solution, and the Dead Sea 22 to 28 per cent. The natural product known as "rock-salt" is the residue left on evaporation of inland seas, such deposits being found in Cheshire, at Stassfurt and Berchtesgaden in Germany, at Vic in France, and at Wieliczka in Galicia. Rock-salt is usually associated with calcium sulphate, alumina, and sandstone. At Stassfurt the layer of rock-salt is covered by another layer of readily soluble salts, technically known as "Abraum" salts, that is, salts which must be removed before the rock-salt is reached.

Rock-salt can be obtained from the salt-deposits either by mining or by making borings through which the salt can be extracted by water. The colour of the mined product varies very much, it may be colourless, yellow, red, grey, or green. Iron is a frequent impurity, and other foreign substances often present are magnesium salts, calcium sulphate, alumina, silica, and so on. The presence of a small proportion of magnesium chloride renders the salt hygroscopic, it must be purified by crystallization.

When the salt is extracted from the deposits by the solution method, two concentric copper tubes are introduced through a boring, the outer tube serving to admit the water, and the inner as a conduit for pumping off the salt solution. The dissolved salt is obtained by evaporation.

The salt found at Droitwich is in natural solution, and is not contaminated with iron. The liquor is pumped to the surface and evaporated.

The concentration of the water of certain mineral springs and of the ocean also affords a means of isolating salt. Less soluble constituents, such as calcium sulphate, separate first. Admixture of the salt with more soluble compounds, such as magnesium chloride, is obviated by not carrying the concentration too far. Shipper⁴ states that the elimination of potassium chloride can be effected by repeated crystallization of the salt from water.

For laboratory use pure sodium chloride is obtained by dissolving the commercial product in water and then drying by saturating the solution with hydrogen chloride. The pure substance can also be prepared by the action of hydrochloric acid on sodium carbonate or hydroxide.

Sodium chloride crystallizes in transparent or opaque cubes,

¹ Baud *J. Physique* 1903 [4] 2 569

² Tammann *Mém Acad St Petersbourg* 1887 [7] 35 No 9 Kohlrausch and von Steinwehr *Sitzungsber K Akad Wiss Berlin* 1902 581 Wilden *Ztschr physikal Chem* 1898 2 49 Arrhenius *ibid* 1892 9 339

³ Guntz *Compt rend* 1883 97 1558

⁴ Shipper *Chem News* 1917 116 213

of the highest intervals of temperature, the times of cooling were rather smaller, and for the two last rather larger than required by the law.

Experiment 3.

As Mr. Leslie found the times of cooling of metallic surfaces considerably enlarged, in moderate elevations of temperature more especially, I took another thermometer having a smaller bulb, and a scale of an inch for 10 degrees, this was treated as in the last experiment, and the results were as under

Thermom. cooled	Bulb clear second	Bulb coated with tinfoil seconds	Log. ratios reduced
From 75° to 65°	in 38	40	40
65 to 55	46	5,	54
55 to 45	54	64	63
45 to 35	63	73	51
35 to 25	80	103	101
25 to 15	130	148	165
15 to 5	310	370	33
	—	—	—
	729	874	871

Here the whole times of cooling, and the several parts are almost accurately as 10 for the vitreous, and as 12 for the metallic surface. They very nearly accord too with the logarithmic ratios. The effect of the metallic surface differs less from that of the vitreous in

lithium, and ammonium has been much debated, but Schaefer¹ demonstrated that sodium chloride forms a complete series of mixed crystals with lithium chloride, and that the work of Kekulé² and Schemtschuschny³ that sodium chloride does not form a completely miscible series of crystals, although the individual crystals tend to separate at 100° C.

For the density of pure sodium chloride Clarke⁴ gives 2.155, Pfeiffer⁵ 2.167 at 17° C.; Kuckmeier⁶ 2.174 at 20° C.; and Haigh⁷ 2.172 at 20° C. Brunner⁸ has investigated the density of the fused salt between its melting-point and 1000° C.

The mean value of several investigations⁹ of the index of refraction of rock-salt at 18° C for the D-line is 1.54432. For the electric conductivity of fused sodium chloride at 960° C Braun¹⁰ gives 0.9206 reciprocal ohms, and at 750° C Poincare¹¹ found 3.339 reciprocal ohms. For the specific heat of the fused chloride between 13° and 46° C Kopp¹² gives 0.213, and from 15° to 98° C Regnault¹³ gives 0.2140. For rock-salt at 0° C Weber¹⁴ gives 0.2146, and from 13° to 45° C Kopp¹⁵ gives 0.219.

As indicated in the table, the solubility of sodium chloride in water is only slightly augmented by rise of temperature.

SOLUBILITY OF SODIUM CHLORIDE

Observer	Tem perature °C	Grams NaCl in 100 grams Water	Observer	Tem perature °C	Grams NaCl in 100 grams Water
Andreae ¹⁶	0	35.63	Earl of Berkeley ¹⁷	90	38.52
"	10	35.69	" "	100	39.12
"	20	35.82	Tilden and Shenstone ¹⁸	118	39.8
"	30	36.03	" "	140	42.1
"	40	36.32	" "	160	43.6
"	50	36.67	" "	180	44.9
"	60	37.06			
"	70	37.51			
"	80	38.0			

¹ Kuckmeier *Zeitsch physikal Chem* 1896 21 53. ¹⁰ Chatelier *Compt rend* 1894, 118 350. Ruff und Pluto *Ber* 1903 36 2357. ¹¹ Puff *Izvustja Polytech Inst St Petersburg* 1906 5. *Chem Zentr* 1906 1 1728. Ostwald *J prakt Chem* 1882 [2] 25 8. Beckhoff *Zeitsch anorg Chem* 1904 40 855.

² Schaefer *Jahrb Min Berl Bd* 1919 43 132.

³ Kurniloff und Schemtschuschny *Izvustja Polytech Inst St Petersburg* 1905 4 227. *Chem Zentr* 1906 1 527.

⁴ *Table Constants of Nature* Washington 1873 1, 30.

⁵ Retgers *Zeitsch physikal Chem* 1889 3 289.

⁶ Kuckmeier *ibid* 1896 21 53. ⁷ Huhh *J Am Chem Soc* 1912 34 1137.

⁸ Brunner *Zeitsch anorg Chem* 1904 38 360.

⁹ Stefan Sielungser K. Akad Wiss Wien 1871 63 [2] 239. Tingley *Ann Chem Phys* 1886 [6] 9-92. Boel *Compt rend* 1895 120 1406. Mutsch *Ann Phys* 1902 [4] 8 139. Duft *Bull Soc franc Min* 1891 14 130.

¹⁰ Braun *Ber* 1874 7 958. ¹¹ Poincaré *Compt rend* 1889 109 174.

¹¹ Kopp *Annalen Suppl* 1864-1865 3 1-289.

¹² Regnault *Pogg Annalen* 1841 53 60 243.

¹³ Weber *Arch Sci phys nat* 1895 [3] 33 590.

¹⁴ Kopp, loc cit. ¹⁶ Andreeae *J prakt Chem* 1884 [2] 29 467.

¹⁵ Earl of Berkely *Phil Trans* 1904 [A] 203 206.

¹⁶ Tilden and Shenstone *ibid* 1884 175 32.

have the thermometer with its bulb in their centers. They were successively filled with boiling water, and suspended in the middle of a room of the temperature 40°, and the times of cooling through each successive 10 degrees were noticed as below.

Water cooled.	Canister covered with paper	Naked canister.	Logarithm, ratios.
From 205° to 195°	in 65 min	10 min	11
195 to 185	7	10.5	12
185 to 175	7.5	11+	13
175 to 165	8+	12	13
165 to 155	9	13.5	14
155 to 145	10	15	16
145 to 135	11.5	17	17
135 to 125	13	19	19
125 to 115	14.5	21.5	22
115 to 105	16	24	25
105 to 95	20	30	29
95 to 85	25	38	35
85 to 75	31	46	44
75 to 65	40	60	60
	—	—	—
	219	327.5	330

Here the results are equally satisfactory and important, not only the times of cooling are in the uniform ratio of 2 to 3 throughout the range, but they almost exactly accord with the logarithmic ratios, indicating the geometric progression in cooling. As experiments of this sort are capable of being repeated by any one without the aid of any expensive instrument or any extraordinary dexterity, it will

sion,¹ electric conductivity² and the effect of other dissolved substances on the solubility.³ Factors to work on the solubility in non-aqueous solvents, and on the compressibility of sodium hydroxide.

Electrolysis.—The electrolysis of sodium chloride is an important technical process, producing caustic alkali and chlorine. As in the chlorine and from its bleaching powder, in the formation of sodium hydroxide, precautions to prevent conversion of the product into hypochlorite and chlorate are necessary.

In one process the cathodic and anodic chambers are separated by a diaphragm of porous clay,⁷ the cathode being a rod of iron to resist the action of the caustic alkali, and the anode being of carbon to withstand the corrosive action of the chlorine.⁸ Hargreaves and Bird⁹ employ a cathode of iron gauze.

In the mercury process the bottom of the electrolytic cell is covered with a layer of mercury into which a non-porous diaphragm dips so that the mercury forms a partition between the anodic and cathodic chamber. The anode is made of carbon, and is immersed in sodium-chloride solution, the cathode is made of iron, and is dipped into water. The mercury acts as cathode, taking up the liberated sodium to form an amalgam, which reacts with the water to produce sodium hydroxide. Various modifications of the process have been devised, one being the substitution of fused sodium chloride for the solution, and of fused lead or tin for mercury, the alloy produced being subsequently decomposed by water.¹⁰

¹ Heimbrodt *Dissertation*, Leipsic, 1903, Graham, *Zeitsch physikal Chem* 1904 50 257

² Kohlrausch and Maltby *Sitzungsber K Akad Wiss Berlin* 1899, 665, Kohlrausch and Grotrian *Pogg Annalen*, 1875, 154, 1, Kohlrausch, Holborn and Diesselhorst *Wied Annalen* 1898 64, 417 Walden, *Zeitsch physikal Chem* 1888 2, 49, Arrhenius *ibid*, 1892, 9 339 Krannhals *ibid*, 1890, 5 250 Schaller *Landolt Bornstein and Meyer hoffer's Tabellen* 3rd ed Berlin 1905, 755, Dégusne *Dissertation* Strasbourg, 1895 Noyes and Coolidge, *Zeitsch physikal Chem* 1903 46 323 Jahn *ibid* 1901 37 673 1907 58 641 Schapire *ibid*, 1904, 49, 513, Hittorf, *Ostwald's Klassiker* 21 23

³ Karsten *Philosophie der Chemie* 1843, Winkelmann, *Ann Physik* 1873 149 492 Mulder *Scherkund Verhandel* 1864 207 van t Hoff and Reicher *Zeitsch physikal Chem* 1889 3 482 Mackenzie *Wied Annalen*, 1877 1, 438 Sestschennoff *Zeitsch physikal Chem* 1889 4 117 Bohr *Wied Annalen* 1899 68 500 Gordon *Zeitsch physikal Chem* 1895 18 1 Roth *ibid*, 1897 24 114 Knopp *ibid* 1904 48 97 Steinr *Wied Annalen* 1894 52 275 Braun *Zeitsch physikal Chem* 1900 33 721 McElvaulin *ibid* 1903 44 600 Geffcken *ibid* 1904 49 257 Rothmund *ibid* 1900 33 401 blitz *ibid* 1903 43 41 Fuller *ibid* 1899 31 360, 1904 49 303 Levin *ibid* 1906 55 513 Dawson *Trans Chem Soc* 1901 79 493 1906 89 605 Abegg and Riesenfeld *Zeitsch physikal Chem* 1902 40 84 Raoult *Ann Chem Phys* 1874 [5] 1 262 Gius *Zeitsch anorg Chem* 1900 25 236 Riesenfeld *Zeitsch physikal Chem* 1902 45 460, Konowaloff *J Russ Phys Chem Soc* 1899 31 910 985 Joannis *Compt rend* 1891 112 393 Fox *Zeitsch physikal Chem* 1902 41 458 Kumpf *Wied Bebl* 1882 6 276 Goodwin *Ber* 1883 15 3039 Kohn and O'Brien *J Soc Chem Ind* 1898 17 1100

⁴ Schiff *Annalen* 1862 118 365 Gerardin *Ann Chem Phys* 1863 [4] 5 146 Iobry de Bruyn *Rei trav chim* 1892 11 147 Linnebarger *Amer Chem J* 1894 16 214

⁵ Richards and Jones *J Amer Chem Soc* 1909 31 158

⁶ Compieg Octte, *Elektrochem Industrie* Stuttgart 1896 112, Forster *Flektrochemie wasseriger Losungen* Leipsic 1905 385

⁷ Haussmann *Zeitsch anorg Chem* 1894 7, 9 Kellner *ibid* 1899 12, 1080

⁸ Forster *Zeitsch Flektrochem* 1900 7 793

⁹ II and Bird *Jahrb Elektrochem* 1895 2 224 compare Forster and Jorre *Zeitsch Elektrochem* 1903 9 206

¹⁰ Compare Haber *Grundriss techn Elektrochem* 1898 469 *Zeitsch Elektrochem* 1903 9, 364 Forster, *Elektrochemie wasseriger Losungen*, Leipsic, 1905 427

$x = \frac{1}{3}$, this gives $1 \frac{1}{3}$, for the whole heat discharged by metal, and $1 \frac{4}{5}$ for that discharged by glass in the same time, where the unit expresses the part conducted, and the fraction the part radiated

That is, from a metallic surface 13 parts of heat are conducted away by the air and 1 part radiated, from a vitreous surface 13 parts are conducted, and 8 parts radiated, in a given time.

The quantity of heat discharged by radiation from the most favourable surface, therefore, is probably not more than 4 of the whole, and that conducted away by the air not less than 6 — Mr Leslie however deduces 57 for the former, and 43 for the latter, because he found the disproportion in the times of cooling of vitreous and metallic surfaces greater than I find it in the lower part of the scale

The obvious consequences of this doctrine in a practical sense are,

1 In every case where heat is required to be retained as long as possible, the vessel should be of metal, with a bright clear surface

2 Whenever heat is required to be given out by a body with as much celerity as possible, the containing vessel, if of metal, ought to be painted, covered with paper, char-

SOLUBILITY OF SODIUM BROMIDE, $\text{NaBr}_{\cdot}2\text{H}_2\text{O}$

Temperature, °C	Grams NaBr in 100 grams Water		Temperature, °C	Grams NaBr in 100 grams Water	
	de Coppet	Étard		de Coppet.	Étard
-20	71.4	57.5	50	116	95
0	79.5	66	60	117	112
10	84.5	72	80	119	113
20	90.3	77	100	121	114
30	97.3	82.5	120	124	116
40	105.8	88	140		118

Meyerhoffer¹ has plotted the solubility curve (fig. 6). The transition-temperature of the dihydrate into the anhydrous salt² (*D*) is 50.674°C , and that of the pentahydrate into the dihydrate (*C*) is -24°C .

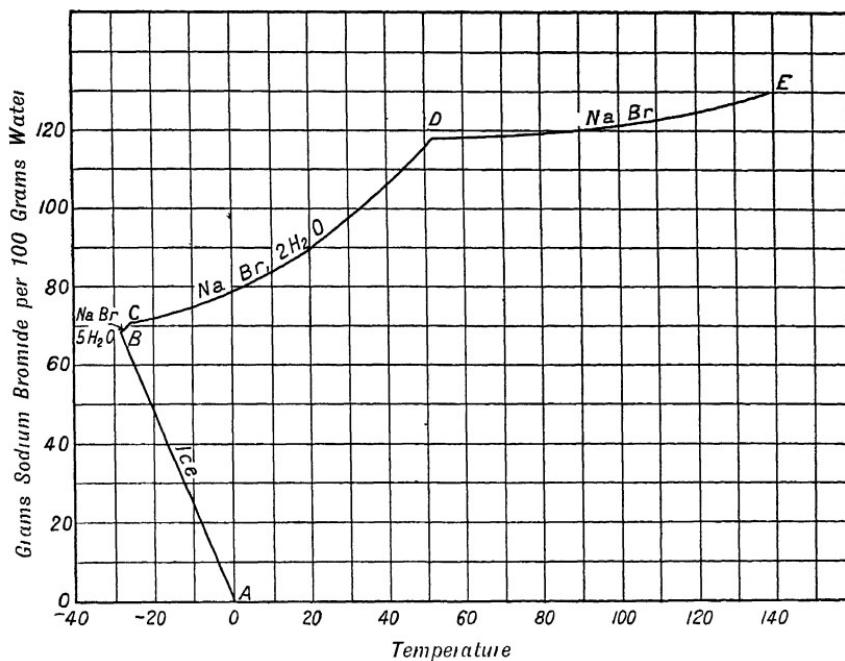


FIG. 6.—Solubility curve of sodium bromide

At its melting point the salt loses only a trace of bromine, but heating with excess of iodine induces a rapid elimination of bromine.³

For the heat of formation of sodium bromide from its elements

¹ Meyerhoffer, *Jandall Bornstein und* Berlin 1905 555

² Richards and Churchill, *Ztsch physikal Chem.* 1899 **28** 314. Richards and Wells, *ibid.* 1906 **56** 348; compare Dawson and Jackson, *Trans Chem Soc.* 1908 **93** 344.

³ Guareschi, *Att R Accad Sci Torino* 1913, **48** 735.

which elapsed whilst the mercury descended from the upper to the under mark were then noted, as under The surrounding air was of a constant temperature

Thermometer immersed	}	cooled in
In carbonic acid gas		112 seconds.
— sulphuretted hydrogen, nitrous oxide, and olefiant	}	100 +
gas.....		
— com air, azotic and oxyg gas	100	
— nitrous gas	90	
— carburet hyd or coal gas	70	
— hydrogen	40	

The refrigerating effect of hydrogen is truly remarkable, I cooled the thermometer 10 times successively in a bottle of hydrogen gas, at each experiment the instrument was taken out, and the stopper put in, till the original temperature was restored, by this, a portion of the hydrogen escaped each time, and an equal portion of common air was admitted, the times of cooling regularly increased as follows, viz 40, 43, 46, 48, 51, 53, 56, 58, 60 and 62 seconds, respectively, at this time the mixture was examined, and found half hydrogen and half common air Equal measures of hydrogen and common air were

Schuller¹ as 0.0881, and between 16° and 99° C. by Regnault² as 0.0868. Thomsen³ gives the heat of formation from the elements as 69.08 Cal., for the heat of solution of the anhydrous salt 1.2 Cal., and for the dihydrate -4.01 Cal.⁴ For the heat of hydration of the anhydrous salt to the dihydrate he gives 5.28 Cal.

The table⁵ indicates the solubility of sodium iodide in water at various temperatures.

Solubility of Sodium Iodide, $\text{NaI} \cdot 2\text{H}_2\text{O}$

Solid Phase, $\text{NaI} \cdot 2\text{H}_2\text{O}$

Temperature, °C	-20	0	10	20	30	40	50	60	65
Grams NaI in 100 g water	148.0	158.7	168.6	178.7	190.3	205.0	227.8	256.8	278.4

Solid Phase, NaI

Temperature, °C	67	70	80	100	120	140
Grams NaI in 100 grams water	293	294	296	302	310	321

The solubility-curve (fig. 7) is in conformity with the existence of a pentahydrate, the transition-point to the dihydrate⁵ (*D*) being -13.5° C.,

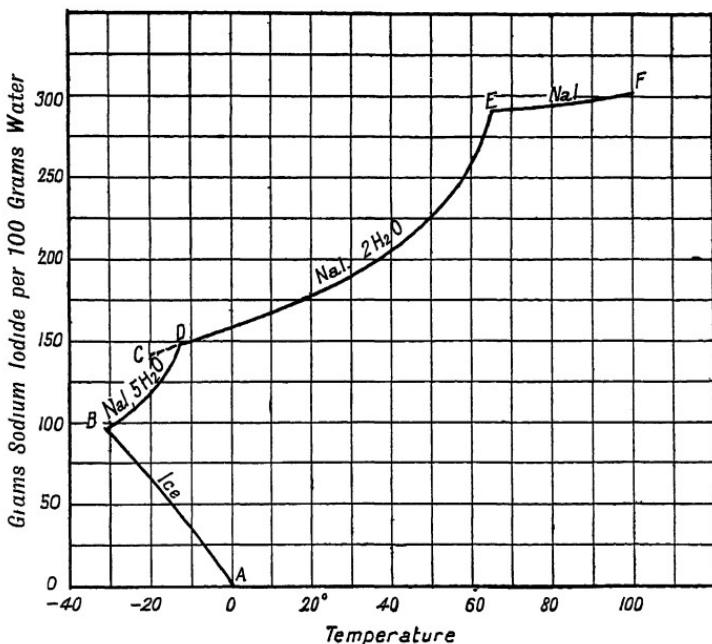


FIG. 7.—Solubility curve of sodium iodide

that of the dihydrate to the anhydrous salt⁶ (*E*) being 65° C. The boiling point of a saturated solution⁷ in contact with the solid is 141° C. At 25° C. 100 grams of ethyl alcohol dissolve 46.02 grams of sodium

¹ Schuller *Pogg Annalen* 1869 136 70 235

² Regnault *Ann Chim Phys* 1841 [3] 1 129

³ Thomsen *Thermochemistry* (Longmans 1908) 49 62 319

⁴ See de Coppel *Ann Chim Phys*, 1883, [5] 30, 420 compare Kremers, *Pogg Annalen* 1856 97 14

⁵ Panfiloff *J Russ Phys Chem Soc* 1893 25 262

⁶ de Coppel *Ann Chim Phys*, 1883 [5] 30 425

⁷ Gerlach *Zeitsch anal Chem*, 1869, 8 285

ter as 1 78, from which he justly infers "this inequality of effect [between atmospheric air and hydrogenous gas] proves its influence to be exerted chiefly, if not entirely, in augmenting the abductive portion."

The expenditure of heat by radiation being the same in hydrogenous gas as in atmospheric air, we may infer it is the same in every other species of gas, and therefore is performed independently of the gas, and is carried on the same in vacuo as in air. Indeed Mr Leslie himself admits that the diminution of the effect consequent upon rarefaction is extremely small, which can scarcely be conceived if air were the medium of radiation.

The effect of radiation being allowed constant, that of the density of the air may be investigated, and will be found, I believe, to vary nearly or accurately as the cube root of the density. In order to compare this hypothesis with observation, let 100 = time of cooling in atmospheric air, the density being 1, then from what has been said above, t will represent the heat lost by a vitreous surface by radiation, and 6 that lost by the conducting power of the medium. Let t = the time of cooling in air of the density d , then if $100 - t = 100t$ t = the heat lost by radiation but the heat conducted away is, by hypothesis, is the time

When the turbid liquid formed by heating the heptahydrate at 20° C is cooled slowly to the ordinary temperature, large greenish-yellow, very deliquescent crystals of the pentahydrate are formed. They melt at 27° C., and are stable at ordinary temperature in absence of air.¹

Sodium hypochlorite is also manufactured by the electrolysis of sodium-chloride solution without a diaphragm (p. 97), the solution being less concentrated than that prepared by the chlorine process from sodium hydroxide, but free from the excess of alkali characteristic of that prepared by the older method.² The process is carried out either in the apparatus designed by Kellner,³ or in that of Haas-Oettel,⁴ sodium chlorate being a by product (*v. infra*). It is noteworthy that electrolysis of sodium-chloride solution with an alternating current also produces sodium hypochlorite.⁵

Thomsen⁶ gives for the heat of formation of sodium hypochlorite in aqueous solution from its elements the value 88.36 Cal., Berthelot⁷ 84.7 Cal. For the molecular depression of the freezing-point in aqueous solution Raoult⁸ found the value 3.38° C.

In aqueous solution sodium hypochlorite finds technical application in the bleaching of paper, linen, cotton, and straw. In direct sunlight, concentrated solutions rapidly lose their activity. Storage in colourless bottles accelerates the rate of decomposition, and in brown bottles retards it. The stability of the solutions is much increased by complete exclusion of light.⁹

Sodium chlorate, NaClO₃.—When chlorine is passed into a hot solution of sodium hydroxide, the hypochlorite primarily formed changes into a mixture of chlorate and chloride, both salts crystallizing out.



The chlorate is purified from the chloride by fractional crystallization. In Muspratt's method¹⁰ magnesium oxide suspended in water is substituted for sodium hydroxide, the solution being concentrated after treatment with chlorine, and sodium carbonate added to precipitate the magnesium for further use. The sodium chlorate crystallizes from the mother-liquor. The salt is also formed from potassium chlorate by double decomposition with substances such as sodium hydrogen tartate and sodium silicofluoride, as well as by the electrolytic decomposition of sodium-chloride solution under certain conditions.¹¹ (p. 97)

Sodium chlorate is a colourless, crystalline substance, and exhibits trimorphism, forming crystals belonging to the cubic, hexagonal,¹² and

¹ Appleby *Trans. Chem. Soc.* 1919 115, 1106.

Forster *Elektrochemie wässriger Lösungen*, Leipzig 1905 341. Engelhardt *Hypochlorite und elekt. Bleiche*, Halle 1903 63. Müller *Zeitsch. Elektrochem.* 1899 5 469. 1900 7 398, 1902 8 909. German Patent 1896 No. 104442.

² Kellner compare Forster loc. cit.

³ Haas Oettel *Zeitsch. Elektrochem.* 1900 7 115. German Patent, 1901, No. 130345. Coppadoro *Gazzetta* 1906 35 11 604.

⁴ Thomsen, *The Electrochemistry* (Longmans 1908) 328.

⁵ Berthelot, *Ann. Chim. Phys.* 1875 [5] 5 338.

⁶ Raoult *Compt. rend.* 1884 98 509.

⁷ Bouvet *Bull. Soc. Pharmacol.* 1917 24 347.

⁸ Muspratt *Dingl. Polytechn. J.* 1884 254 17.

¹⁰ Forster, *Elektrochemie wässriger Lösungen*, Leipzig 1905 341. Engelhardt, *Hypochlorite und elekt. Bleiche*, Halle, 1903, 63.

¹² Retgers, *Zeitsch. Kryst. Min.*, 1894 23, 266.

if $100'' \cdot 4 :: 40'' \cdot 16 =$ the heat lost by radiation in that gas in 40 seconds ; whence .84 = the heat conducted away by the air in 40", or .021 per second , but in common air the loss per second by abduction is only .006 ; from this it appears that the refrigerating power of hydrogenous gas is $3\frac{1}{2}$ times as great as that of common air

It may be asked what is the cause why different gases have such different cooling effects, especially on the supposition of each atom of all the different species possessing the same quantity of heat? To this we may answer that the gases differ from each other in two essential points, in the number of atoms in a given volume, and in the weight or inertia of their respective atoms Now both number and weight tend to retard the motion of a current that is, if two gases possess the same number of particles in a given volume, it is evident that one will disperse heat most quickly which has its atoms of the least weight , and if other two gases have particles of the same weight, that one will most disperse heat which has the least number in a given volume , because the resistance will be as the number of particles to be moved, in like circumstances Of the gases that have nearly the same number of particles in the same volume, are, hydrogen,

the decomposition with evolution of oxygen, there is a partial conversion of the salt into perchlorate and chloride.



The salt can also be prepared by neutralizing perchloric acid with sodium hydroxide, but it is manufactured by the electrolytic oxidation of a 25 per cent sodium-chlorate solution at 10° C, platinum electrodes and a high anode-potential being employed¹. This process finds application in the manufacture of potassium perchlorate, this salt being obtained from the sodium compound by the action of potassium chloride.

At ordinary temperature sodium perchlorate crystallizes as the very deliquescent monohydrate, but above 50° C as the anhydrous salt². Its deliquescent character hinders its technical application. The melting-point³ of the anhydrous salt is 482° C. On heating, it is decomposed into chloride and oxygen, a proportion of chlorate being simultaneously formed⁴. From cryoscopic experiments with sodium sulphate as solvent, Lowenherz⁵ inferred the molecular formula to be NaClO_4 .

For the heat of formation⁶ from its elements, Berthelot gives 100.3 Cal., and for the heat of solution⁷ at 10° C, 3.5 Cal. The electric conductivity has been investigated by Ostwald⁸ and by Walden⁹.

Sodium hypobromite, NaOBr —When bromine reacts with sodium hydroxide in aqueous solution, sodium hypobromite is formed.



It is also a product of the electrolysis of sodium bromide without a diaphragm¹⁰ (p. 103).

The salt has only been obtained in solution. In this form it is an important oxidizer in analytical operations. For the heat of formation of the dissolved compound from its elements, Berthelot¹¹ gives 82.1 Cal.

Sodium bromate, NaBrO_3 —The bromate is formed by the action of bromine on a hot solution of sodium hydroxide, but is best obtained by the electrolysis of sodium bromide under certain conditions.

Like the chlorate, sodium bromate is trimorphous, crystallizing in the cubic,¹² hexagonal, and rhombic¹³ systems. Its melting point¹⁴ is 381° C. For the density Kremers¹⁵ gives 3.339, and Le Blanc and Rohland¹⁶ 3.254. At 20° C, 100 grams of water dissolve 38.8 grams, and at 100° C, 91 grams.¹⁷ The boiling point of the saturated solution in contact with the solid is 109° C. The compound finds application as an oxidizer.

References are appended to investigations of its optical properties¹⁸.

¹ Winteler *Zeitsch Physiol Chem* 1898 5 218 Forster, *ibid* 1898 4 386
Potulitzer, *J Russ Phys Chem Soc* 1889 I 258

² Cannell and O'Shea *Trans Chem Soc* 1884 45 409

³ Scobur *Zeitsch physikal Chem* 1903 44 319

⁴ Lowenherz *ibid* 1895 I 8 70, compare Curtis *Trans Chem Soc* 1895 74 593

⁵ Berthelot *Ann Chem Phys* 1882 [5] 27 218

⁶ Berthelot *ibid* 1875 [5] 4 103

⁷ Ostwald *Lehrbuch der allgm Chem* 2nd ed., Leipzig, 1893, 743

⁸ Walden *Zeitsch physikal Chem* 1888 2 49

¹⁰ Forster *Physikalische wasserige Losungen* Leipzig, 1905 341

¹¹ Berthelot *Ann Chem Phys* 1877 [5] 10 19

¹ Reitgers *Zeitsch Kryst Min* 1894 23 266

¹³ Brauns *Jahrb Min*, 1898 I 40

¹⁴ Cannell and Williams, *Trans Chem Soc* 1880 37 125

¹ Kremers *Pogg Annalen* 1856 99 443

¹⁶ Le Blanc and Rohland, *Zeitsch physikal Chem* 1896 19 261

¹⁷ Kremers *Pogg Annalen* 1855 97 5

¹⁸ Traube *Landolt, Bornstein, and Meyerhoffer's Tabellen*, 3rd ed. Berlin 1905 706

of great and extraordinary commotion in the atmosphere, and is at most of a very short duration. What then is the occasion of this diminution of temperature in ascending? Before this question can be solved, it may be proper to consider the defects of the common solution — Air, it is said, is not heated by the direct rays of the sun, which pass through it as a transparent medium, without producing any calorific effect, till they arrive at the surface of the earth. The earth being heated, communicates a portion to the contiguous atmosphere, whilst the superior strata in proportion as they are more remote, receive less heat, forming a gradation of temperature, similar to what takes place along a bar of iron when one of its ends is heated.

The first part of the above solution is probably correct. Air, it should seem, is singular in regard to heat, it neither receives nor discharges it in a radiant state, if so, the propagation of heat through air must be effected by its conducting power, the same as in water. Now we know that heat applied to the under surface of a column of water is propagated upwards with great celerity, by the actual ascent of the heated particles. It is equally certain too that heated air ascends. From these observations it should follow that the

Solubility of Sodium Periodate.

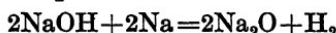
Temperature, °C	0	25	40	100
Grams of $\text{Na}_2\text{H}_3\text{IO}_6$ in 100 g. of solution	0.104	0.157	0.187	0.434

A cold, aqueous solution of sodium hydroxide converts this salt into the periodate of the formula $\text{Na}_3\text{H}_2\text{IO}_6$. These two substances are the only periodates of sodium known to exist in aqueous solution. The optical properties¹ and electric conductivity in aqueous solution² of the disodium salt have been investigated.

Other periodates have been described by Walden³ and by Muller⁴.

Sodium manganate and permanganate—The modes of preparation and the properties of sodium manganate and permanganate are given in Vol. VIII.

Sodium monoxide, Na_2O —The monoxide is produced by combustion of sodium in dry air, the peroxide being formed simultaneously, or by heating the hydroxide or peroxide with sodium.⁴



Sodium monoxide is a white substance when cold, pale-yellow when hot, and melts at bright redness. It is very hygroscopic, combining with water to form the hydroxide, the heat evolved being 56.5 Cal.⁵ For the density Beketoff⁶ gives 2.314, and Rengade⁷ 2.27. The heat of formation from the elements is 100.7 Cal.⁸ Above 400° C it yields equimolecular proportions of sodium and sodium peroxide. It is converted by hydrogen into an equimolecular mixture of sodium hydroxide and hydride, and it also combines with fluorine, chlorine, and iodine.

The so called "sodium suboxide," obtained by combustion of sodium in a limited supply of oxygen, seems to be either a mixture or solid solution of sodium and sodium monoxide.

Sodium peroxide, Na_2O_2 —The peroxide is manufactured by the action of dry air, free from carbon dioxide, on sodium⁹ in an iron tube at 300° C,¹⁰ the only process employed for its production on the large scale. The commercial article contains about 98 per cent of sodium peroxide.

Sodium peroxide has a yellowish colour. It is not decomposed by heat, but is a very powerful chemical reagent, in many respects resembling hydrogen peroxide.

It can act as a reducer,¹¹ decomposing salts of silver, gold, and mercury, with evolution of oxygen. As an oxidizer, it reacts energetically with silver, tin, and lead. It converts the oxides of carbon into sodium carbonate, and nitrogen monoxide and nitric oxide into sodium nitrate. It is reduced to sodium¹² by charcoal or carbides of the alkaline earth-

¹ Groth *Pogg Annalen* 1869 137 433

Walden *Zeitsch physikal Chem.*, 1888 2 49

² Muller *Zeitsch Elektrochem.* 1901 7, 509, 1904 10 49

³ Badische Anilin und Soda Fabrik, German Patent No. 147933. Rengade, *Compt rend.*, 1906 143 1152 1907 144 753, *Ann Chim Phys.* 1907 [8] 11 424

Rengade *Compt rend.* 1908 146, 129, *Bull Soc chim.* 1908 [4] 3 190, 194

⁴ Beketoff *J Russ Phys Chem Soc* 1887 1, 57

⁵ Rengade, *Compt rend.*, 1906 143 1152 1907, 144 753 *Ann Chim Phys.* 1907 [8] 11 424

⁶ Rengade, *Compt rend.*, 1908, 146, 129, *Bull Soc chim.*, 1908 [4] 3 190 194

de Forcand, *Compt rend.*, 1914 158, 991

⁷ Castner, *J Soc Chem Ind.* 1892 11, 1005, compare Gay Lussac and Thénard *Recherches physico chimiques* Paris, 1811

⁸ Castner, *British Patent*, 1891, No. 20003

⁹ Poleck, *Ber.*, 1894, 27 1051

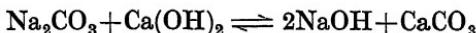
¹⁰ Bamberger, *Ber.*, 1898, 31, 54

It is an established principle that any body on the surface of the earth unequally heated is observed constantly to tend towards an equality of temperature, the new principle announced above, seems to suggest an exception to this law. But if it be examined, it can scarcely appear in that light *Equality of heat and equality of temperature*, when applied to the same body in the same state, are found so uniformly to be associated together, that we scarcely think of making any distinction between the two expressions No one would object to the commonly observed law being expressed in these terms *When any body is unequally heated, the equilibrium is found to be restored when each particle of the body becomes in possession of the same quantity of heat* Now the law thus expressed is what I apprehend to be the true general law, which applies to the atmosphere as well as to other bodies It is an *equality of heat*, and not an *equality of temperature* that nature tends to restore

The atmosphere indeed presents a striking peculiarity to us in regard to heat we see in a perpendicular column of air, a body without any change of form, slowly and gradually changing its capacity for heat from a less

de Forcrand¹ mentions two other sodium peroxides, Na_2O_3 and Na_2O_4 . The heat of formation of the first from the elements is given as approximately 126.7 Cal., and of the second as approximately 130 Cal.

Sodium hydroxide, NaOH . The pure hydroxide can be prepared in the laboratory by dissolving sodium in water and evaporating the solution,² or by the electrolysis of commercial sodium hydroxide in aqueous solution with a mercury cathode, the amalgam formed being decomposed by water.³ A solution free from carbonate can be obtained in the laboratory by suspending metallic sodium in a layer of ether floating on the surface of water. The metal dissolves slowly in the water present in the ether, and the sodium hydroxide passes into the bottom aqueous layer.⁴ The hydroxide is manufactured by the electrolysis of a solution of sodium chloride (p. 97), and, according to van Laer,⁵ an economical yield can be obtained directly by the electrolysis with a suitable diaphragm of a solution of sodium carbonate containing nitrate or sulphate of sodium to hinder the formation of sodium hydrogen carbonate. Sodium hydroxide is also produced industrially by the much older method of decomposing sodium carbonate with slaked lime, a reversible reaction.⁶



The solution of sodium hydroxide is evaporated in iron vessels, the finished product being marketed in the form of sticks or powder, or in cylindrical blocks of about 6½ cwt enclosed in iron drums. Slaked lime also decomposes sodium sulphate with production of sodium hydroxide, and the effect on the yield of the temperature and the dilution of the solution has been studied by Neumann and Karwat.⁷

Sodium hydroxide is a white substance of density⁸ 2.130. It dissolves readily in both water and alcohol. It is very stable, melting⁹ at 318.4° C. and at a higher temperature volatilizing without decomposition. Admixture with other substances lowers the melting point.¹⁰ The mixture containing 58.4 per cent of potassium hydroxide melts at 167° C., that with 20.7 per cent of a mixture of 48.5 per cent of sodium carbonate and 51.5 per cent of potassium carbonate at 265° C., and that with 17 per cent of sodium carbonate at 280° C. For the latent heat of fusion per mol., Hevesy¹¹ gives 1.602 Cal. Its hygroscopic character causes it to liquefy on exposure to air, but it is converted into solid carbonate by the action of atmospheric carbon dioxide. The percentage of water in fused samples varies between 0.9 and 1.2, the average being 1.1.¹²

¹ de Forcrand *Compt. rend.* 1914 **158** 843, 991.

Compare Kuster *Zeitsch. anorg. Chem.* 1901 **41** 471.

² Jonissen and Filippo *Chem. Weekblad* 1909 **6** 145.

³ Cornog *J. Amer. Chem. Soc.* 1921 **43** 2573.

van Laer *J. Chim. phys.* 1917 **15** 154.

⁴ Bodlandr *Zeitsch. Elektrochem.* 1905 **12** 186; Ic Blinc and Novotny *Zeitsch. anorg. Chem.* 1906 **51** 181; 1907 **53** 347; Wegscheider und Walter *Annalen* 1907 **351** 87; *Monatsh.* 1907 **28** 543, 555, 633.

⁵ Neumann and Karwat *Zeitsch. Elektrochem.* 1921 **27** 114.

⁶ Filhol *Ann. Chim. Phys.* 1847 [3] **21** 415.

⁷ Hevesy *Zeitsch. physikal. Chem.* 1910 **73** 667.

⁸ Neumann and Bergvæ *Zeitsch. Elektrochem.* 1914 **20** 271.

⁹ Hevesy *Zeitsch. physikal. Chem.* 1910 **73**, 667.

¹⁰ Wallace and Fleck *Trans. Chem. Soc.*, 1921 **119** 1839.

reduced to the same temperature as the surrounding air ; or vice, versa, if two measures of air at the proposed height were condensed into one measure, their temperature would be raised 50° , and they would become the same in density and temperature, as the like volume of air at the earth's surface. In like manner we may infer, that if a volume of air from the earth's surface, to the summit of the atmosphere were condensed and brought into a horizontal position on the earth's surface, it would become of the same density and temperature as the air around it, without receiving or parting with any heat whatever

Another important argument in favour of the theory here proposed may be derived from the contemplation of an atmosphere of vapour Suppose the present aerial atmosphere were to be annihilated, and one of steam or aqueous vapour were substituted in its place , and suppose further, that the temperature of this atmosphere at the earth's surface were every where 212° and its weight equal to 30 inches of mercury Now at the elevation of about 6 miles the weight would be 15 inches or $\frac{1}{2}$ of that below, at 12 miles, it would be 7 5 inches, or $\frac{1}{4}$ of that at the surface, &c and the temperature would probably diminish 25° at each of those intervals It could not di-

monohydrate melts at 64.3°C . For its density Gerlach¹ gives 1.829. At 12°C it is transformed² into the dihydrate, which at a concentration of 45.5 per cent. of sodium hydroxide is in equilibrium at 5°C with a 3.5 hydrate, $2\text{NaOH} \cdot 7\text{H}_2\text{O}$, as is also the α -tetrahydrate at the same temperature and a concentration of 32 per cent. of sodium hydroxide. At -17.7°C the α -tetrahydrate changes to the pentahydrate, and this form at -24°C to the heptahydrate. The saturated solution in contact with the solid boils at 814°C ³.

The specific heat of the anhydrous hydroxide is given by Blümcke⁴ as 0.78 between 0° and 98°C . The mean molecular refraction of the molten hydroxide between 320° and 440°C is 5.37⁵. The heat of formation from the elements is given by de Forcrand⁶ as 103.10 Cal., and that from the solid monoxide and liquid water as 36.50 Cal. For the former, Rengade⁷ gives 101.9 Cal., and in solution 111.8 Cal., for the heat of formation in dilute solution from sodium and water he gives 44.1 Cal. The heat of solution is given by Thomsen⁸ as 9.94 Cal., and by Berthelot⁹ as 9.8 Cal. The heat of dilution has also been studied by both these investigators. The heat of formation of the monohydrate is given by Berthelot as 3.25 Cal. The heat of neutralization of the hydroxide by mineral acids has been investigated by Richards and Rowe¹⁰.

At ordinary temperatures an aqueous solution of sodium (or potassium) hydroxide dissolves sulphur, forming sulphide, polysulphides, thiosulphate, and sulphite. The reaction is very complex, but Calcagni¹¹ thinks that the sulphide is probably formed first, thiosulphate next, and then polysulphides. Finally, sulphite is produced by decomposition of the thiosulphate. With concentrated solutions part of the sulphur probably dissolves without entering into combination. Ammonium hydroxide of density 0.888 behaves similarly¹¹.

When heated in copper vessels at temperatures between 350° and 600°C in contact with air, sodium hydroxide has been observed to dissolve up to 0.73 per cent. of its weight of copper. The action on iron is less, and on nickel least of all¹².

Other properties of aqueous solutions have been studied, such as the density,¹³ vapour pressure,¹⁴ boiling point,¹⁵ molecular depression of the freezing point,¹⁶ electric conductivity,¹⁷ electrolytic dissociation,¹⁸

¹ Gerlach *Jahrsbericht* 1886 69. Compare Hermes, *Annalen* 1861 119 170.

² Gerlach, *Zeitsch anal Chem* 1887 26 413.

³ Blumcke, *Wied Annalen* 1885 25 417.

⁴ G. Meyer and Heck *Zeitsch Elektrochem* 1922 28, 21.

⁵ de Forcrand *Ann Chim Phys* 1908 [8] 15 433.

⁶ Rengade, *Compt rend*, 1908, 146 129. *Bull Soc chim* 1908 [4] 3 190 194.

⁷ Thomsen *Thermochimistry* (Longmans 1908) 49.

⁸ Berthelot, *Ann Chim Phys* 1875 [5] 4 521.

⁹ Richards and Rowe *J Amer Chem Soc* 1922 44 684.

¹⁰ Calcagni *Gazzetta* 1920 50 II 331.

¹¹ Wallace and Flecl *Trans Chem Soc* 1921 119 1839.

¹² Pickering *Trans Chem Soc* 1893 63 890. Forch *Wied Annalen* 1895 55 100. Wegscheider and Walter *Monatsh* 1906 27 13.

¹³ Diederich, *Wied Annalen* 1891 42 513. Tammann *ibid* 1885 24 530. *Mem Acad St Petersbourg* 1887 [7] 35 No 9.

¹⁴ Gerlach *Zeitsch anal Chem* 1887 26 413.

¹⁵ Loomis *Wied Annalen* 1897 66 532.

¹⁶ Loomis, *loc cit* Kohlrausch and Holborn *Leitvermögen der Elektrolyte* Leipzig 1898, Foster *Physical Rev* 1899 8 257. Demolis *J Chim phys* 1906 4 526. Kunz *Zeitsch physikal Chem* 1903 42 591. Bein *ibid* 1898 27 I 28 439. Kuschel *Wied Annalen* 1881 13 289.

¹⁷ Arrhenius, *Zeitsch physikal Chem*, 1892, 9 1339.

a perfect equilibrium having once obtained, there could be neither condensation nor evaporation in any region. For every 400 yards of elevation, the thermometer would descend 1 degree

2 If the atmosphere were constituted just as above, except that the temperature now diminished more rapidly than at the rate of 25° for 6 miles, then the temperature of the higher regions not being sufficient to support the weight, a condensation must take place; the weight would thus be diminished, but as the temperature at the surface is always supposed to be kept at 312° , evaporation must go on there with the design to keep up the pressure at 30 inches. Thus there would be perpetual strife between the recently raised vapour ascending, and the condensed drops of rain descending. A position much less likely than the preceding one

3 The same things being supposed as before, but now the temperature decreases more slowly than at the rate of 25° for 6 miles in this case the density of the steam at the earth's surface would be a maximum for the temperature, but nowhere else, so that if a quantity of water were taken up to any elevation it would evaporate, but the increased weight of the atmosphere would produce a condensation of

Four hydrates have been described by Parravano and Fornaini,¹ containing respectively 9, 6, 5½, and 5 molecules of water. The penta-hydrate was also prepared by Böttger² by adding alcohol to a solution of sodium hydroxide saturated with hydrogen sulphide. Sabatier³ mentions a 4½-hydrate, obtained by drying the 9-hydrate over sulphuric acid.

The solution of the sulphide in water has an alkaline reaction due to hydrolytic dissociation. Atmospheric oxygen converts the dissolved sulphide into thiosulphate, and electrolytic oxidation yields the sulphate. The solution dissolves sulphur, forming polysulphides.

The melting-point of sodium monosulphide is 920° C.⁴ For the anhydrous salt the density is given by Filhol⁵ as 2.471, a modern determination by Rengade and Costeanu⁶ being 1.856. The heat of formation from its elements is given by Sabatier⁷ as 88.2 Cal., and by Rengade and Costeanu⁸ as 89.7 Cal. The investigators last mentioned found the heat of solution to be 15.5 Cal. The heat of hydration of the anhydrous salt to the 9 hydrate is 31.72 Cal. For the heat of formation in aqueous solution from the elements, Thomsen⁹ gives 101.99 Cal.

In aqueous solution sodium monosulphide reacts with iodine to form sodium iodide, the liberated sulphur dissolving in excess of the sulphide solution.¹⁰ A double sulphide of the formula $\text{Na}_2\text{S}, \text{Cu}_2\text{S}$ has been prepared.¹¹ It melts at 700° C.

Other investigations of solutions of sodium sulphide include the concentration of the hydroxyl-ions and the depression of the freezing-point,¹² the solubility of ammonia,¹³ and the density.¹⁴

Sodium polysulphides¹⁵—According to Thomas and Rule,¹⁶ the whole series of polysulphides Na_2S_x exists, x being a whole number with the maximum value 5. Their results obtained by the ebullioscopic method in alcoholic solution favour the simple formula Na_2S_x as against Na_4S_x . On the other hand, Friedrich¹⁷ claims to have prepared polysulphides with the formulæ indicated, the melting points being given in brackets: Na_4S_3 (772° C.), Na_2S_2 (445° C.), Na_4S_5 (345° C.), Na_2S_3 (320° C.), Na_4S_7 (295° C.), Na_2S_4 (255° C.), Na_4S_9 (210° C.), and probably Na_2S_5 (185° C.).

Bloch and Hohn¹⁸ have prepared solutions containing the *disulphide* Na_2S_2 , *trisulphide* Na_2S_3 , *tetasulphide* Na_2S_4 , and *pentasulphide* Na_2S_5 .

¹ Parravano and Fornaini *Atti R Accad Lincei* 1907 [5] 16 II 464 *Gazzetta*, 1907 37 II 521

² Böttger *Annalen* 1884 223 335

³ Sabatier *Ann Chim Phys* 1881 [5] 22 66

⁴ Friedrich *Metall und Erz* 1914 II 79

Filhol *Ann Chim Phys*, 1887 [3] 21, 415

Rengade and Costeanu *Compt rend* 1914 158 946

Sabatier *Ann Chim Phys* 1881 [5] 22 1

Rengade and Costeanu *loc cit*

Thomsen *Thermochemistry* (Longmans 1908) 322

Friehlich *Zeitsch anal Chem* 1918 57 21

¹¹ Friehlich *loc cit*

¹ Kuster and Heberlein *Zeitsch anorg Chem* 1905 43 53 compare Kolichen *Zeitsch physikal Chem* 1900 33 173 Knox *Zeitsch Fleischchem* 1906 12 477

¹³ Abegg and Riesenfeld *Zeitsch physikal Chem* 1902 40 84 Rioult *Ann Chim Phys* 1874 [5] I 262 Grus *Zeitsch anorg Chem* 1900 25 236

¹⁴ Bock *Wied Annalen* 1887 30 631

¹ On the constitution of the polysulphides see this series Vol VII Kuster *Zeitsch anorg Chem* 1905 44 431 46 113 Kuster and Heberlein *ibid* 1905 43 53

¹⁶ Thomas and Rule *Trans Chem Soc* 1917 III 1063

¹⁷ Friehlich, *loc cit*

¹⁸ Bloch and Hohn *Ber* 1908 41 1961

That an atmosphere of steam does actually surround the earth, existing independently of the other atmospheres with which however it is necessarily most intimately mixed, is I think capable of demonstration I have endeavoured to enforce and illustrate it in several Essays in the Memoirs of the Manchester Society, and in Nicholson's Journal, to which I must refer Now an atmosphere of any elastic fluid, whether of the weight of 30 inches of mercury, or of half an inch, must observe the same general laws, but it should seem that an atmosphere of vapour varies its temperature

condensations, though it may be nearly so for most of them towards the conclusion, the space occupied by the solid atom or particle bears a considerable proportion to the whole space occupied by it and its atmosphere At the first compression, the atmosphere of heat might be said to be reduced into half the space, but at the last, the reduction would be much greater, and therefore more heat given out than determined by theory

Since writing the above Mr Fwirt informs me that the idea respecting steam, which I had from him, is originally Mr Watt's In Black's Lectures, Vol 1 page 190, the author, speaking of Mr Watt's experiments on steam at low temperatures, observes, " we find that the latent heat of the steam is at least as much increased as the sensible heat is diminished " It is wonderful that so remarkable a fact should have been so long known and so little noticed

It is a white, crystalline solid, very deliquescent, freely soluble in water, and moderately soluble in alcohol. When exposed to air it evolves hydrogen sulphide,¹ and is completely decomposed by heat into this gas and sodium monosulphide.² The anhydrous salt is also obtained by the interaction at 300° C of sodium monosulphide and hydrogen sulphide free from carbon dioxide and oxygen.³ Sabatier's⁴ method is to saturate a solution of sodium sulphide with hydrogen sulphide, and concentrate in an atmosphere of the same gas. A solution can be obtained by saturating sodium-hydroxide solution with hydrogen sulphide. A dihydrate and a trihydrate have been described.⁵

The heat of formation of the solid from the elements is given by Sabatier as 55.7 Cal., that in solution by Thomsen⁶ as 58.48 Cal., and by Berthelot⁷ as 60.7 Cal. For the heat of solution of the anhydrous salt at 17.5° C Sabatier gives 4.4 Cal., and for that of the dihydrate -1.5 Cal., it follows that the heat of hydration of the dihydrate is 5.9 Cal.

The preparation in solution of a compound of the formula NaOSH has been described by Gutmann.⁸

Sodium sulphite, Na₂SO₃.—The anhydrous sulphite can be prepared by heating equimolecular proportions of sodium hydrogen sulphite and sodium hydrogen carbonate.⁹



It is also precipitated by the action of ammonia on a solution containing sodium chloride and ammonium sulphite in equimolecular proportions.¹⁰ Hartley and Barrett¹¹ have described a method of preparation from sulphur dioxide and sodium carbonate. It is a white, crystalline salt.

For the solubility of this substance in 100 grams of water at 20° C Kremers¹² gives 28.7 grams, at 40° C, 49.5 grams, and at 100° C Fourcroy¹³ gives 38 grams. At 10° C the heat of solution¹⁴ of the anhydrous salt is 2.5 Cal.

Hartley and Barrett¹¹ state that the only stable forms are the anhydrous salt and the heptahydrate, Na₂SO₃.7H₂O. Neither they nor Schultz-Sellack¹⁵ could isolate the decahydrate described by Muspratt.¹⁶ The anhydrous salt belongs to the hexagonal system, and at 15° C has the density 2.6334. The heptahydrate is monoclinic, its density at 15° C being 1.5939. At 10° C the heat of solution of the heptahydrate according to de Forerand¹⁷ is -11.1 Cal., and the heat of hydration 13.6 Cal.

¹ Rule *Trans Chem Soc* 1911, 99 558

Thomus and Rule *ibid* 1913 103 871

² Verein Chemischer Fabriken in Mannheim *German Patent*, 1908 No 194882

³ Sabatier *Ann Chim Phys* 1881 [5] 22 15

Bloxam *Trans Chem Soc* 1900 77 753

⁴ Thomsen *Thermochemistry* (Longmans 1908) 322

⁵ Berthelot *Ann Chim Phys* 1875 [5] 4 106

⁶ Gutmann *Ber* 1908 41 3351

⁷ Payello and Sivler *German Patent* No 80390

¹⁰ Diesel and Lennhof *ibid* No 80185 compare Duvieusart *ibid* 1909 No 210804

¹¹ Hartley and Barrett *Trans Chem Soc* 1909 95, 1178

¹² Kremers *Pogg Annalen* 1856 99 50

¹³ Fourcroy *Compte Rendu des Séances de l'Académie des Sciences* Paris 1896 122 464

¹⁴ de Forerand *Ann Chim Phys* 1884 [6] 3 243

¹⁵ Schultz Sellack *J prakt Chem*, 1870 [2], 2, 459

¹⁶ Muspratt, *Phil Mag*, 1847, [3], 30, 414

1 The specific gravity of ice is less than that of water in the ratio of 92 to 100.

2 When water is exposed in a large suspended jar to cool in still air of 20 or 30°, it may be cooled 2 or 3° below freezing, but if any tremulous motion take place, there appear instantly a multitude of shining hexangular *spiculae*, floating, and slowly ascending in the water.

3 It is observed that the shoots or ramifications of ice at the commencement, and in the early stage of congelation are always at an angle of 60 or 120°.

4 Heat is given out during congelation, as much as would raise the temperature of water 150° of the new scale. The same quantity is again taken in when the ice is melted. This quantity may be $\frac{1}{4}$ of the whole heat which water of 32° contains.

5 Water is densest at 36° of the old scale, or 38° of the new. From that point it gradually *expands* by cooling or by heating alike, according to the law so often mentioned, that of the square of the temperature.

6 If water be exposed to the air, and to agitation, it cannot be cooled below 32°, the application of cold freezes a part of the water, and the mixture of ice and water requires the temperature of 32°.

solution, an illustration of his difficulty being the identity in their electric conductivities. Since both isomerides might yield the same ions, Barth's evidence is inconclusive, but his work on the mercury salts appears to confirm the assumption of the sulphonic formula.

Schwicker claimed to have prepared distinct derivatives by the action of ethyl iodide, but a repetition of his work by Fraps¹ led to negative results. Arbusoff² investigated the interaction of methyl iodide and the double sulphites obtained by Schwicker's method, the sodium atom in each instance being replaced by a methyl group, with formation of the same compound,



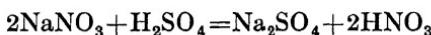
If two isomerides do exist, that with potassium attached directly to sulphur must be unstable, and change readily into the isomeric form³

Sodium pyrosulphite, $\text{Na}_2\text{S}_2\text{O}_5$ —When excess of sulphur dioxide is passed into sodium-carbonate solution at low temperature, anhydrous sodium pyrosulphite separates⁴, at ordinary temperature the hydrate $\text{Na}_2\text{S}_2\text{O}_5 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ is formed⁵. This substance may be regarded as an anhydride of sodium hydrogen sulphite $2\text{NaHSO}_3 - \text{H}_2\text{O} = \text{Na}_2\text{S}_2\text{O}_5$. The heat of formation of the anhydrous salt from its elements is given by de Forcand⁶ as 348.4 Cal, and the heat of solution at 10° C as 5.2 Cal. The electric conductivity has been investigated by Walden⁷. The salt is employed to retard oxidation of photographic developers.

Sodium sulphate, Na_2SO_4 —The sulphate is often called "Glauber's salt," on account of its application in the seventeenth century as a medicine by the physician Glauber, the specific being known as "sal mirabile Glauberi." Its purgative action seems to be a phenomenon dependent on osmosis.

The anhydrous sulphate is a constituent of oceanic salt deposits, and is called *thenardite*. An isomorphous mixture with potassium sulphate is known as *glasenite*, a double salt with magnesium sulphate as *astrakanite*, and with calcium sulphate as *glauberite*.

Sodium sulphate is an intermediate product in the manufacture of sodium carbonate by the Le Blanc process (p. 143). It is also a by-product in the manufacture of nitric acid by the interaction of sodium nitrate and sulphuric acid.⁸



In the Stassfurt deposits sodium chloride and magnesium sulphate monohydrate or *kieserite* are present, and on cooling the solution to -3° C sodium sulphate crystallizes out. A mixture of sodium chloride, magnesium sulphate, and sand also reacts at dull red heat to form

¹ Fraps *Amer. Chem. J.*, 1900, 23, 202.

Arbusoff *J. Russ. Phys. Chem. Soc.* 1909, 41, 447, compare Godby *Proc. Chem. Soc.* 1907, 23, 241.

³ Garritt (*Trans. Chem. Soc.* 1915, 107, 1324) measured the molecular extinctions of solutions of the isomerides but found no selective absorption, so that his method gave inconclusive results.

⁴ Schultz *Pogg. Annalen* 1868, 133, 137, compare Carey and Hurter, *British Patent*, 1882, No. 4512.

⁵ Rohring *Gmelin Kraut*, and Friedheim's *Handbuch der anorg. Chem.* 7th ed. 1906, 2, 1, 321.

⁶ de Forcand *Ann. Chim. Phys.* 1884 [6], 3, 243.

⁷ Walden, *Zeitsch. physikal. Chem.*, 1887, 1, 529.

⁸ See this series, Vol. VI.

stratum of particles placed upon these in like order of squares, but so that each globule falls into the concavity of four others on the first stratum, and consequently rests upon four points, elevated 45° above the centres of the globules A perpendicular section of such globule resting upon two diagonal globules of the square is exhibited in Fig 3 Conceive a third stratum placed in like manner upon the second, &c. The whole being similar to a square pile of shot —The above constitution is conceived to represent that of water at the temperature of greatest density

To find the number of globules in a cubic vessel, the side of which is given , let n = the number of particles in one line or side of the cube , then n^3 is the number in any horizontal stratum , and because a line joining the centres of two c ' , ~ particles in different strata makes an angle of 45° with the horizontal plane, the number of strata in the given height will be $n - \sin \text{e of } 45^\circ = n - \frac{1}{2}\sqrt{2}$ Whence the number of particles in the cubic vessel $= n^3 - \frac{1}{2}\sqrt{2} = n^3\sqrt{2}$

Now let it be supposed that the square pile is instantly drawn into the shape of a rhombus (Fig 2), then each horizontal stratum will still consist of the same number of particles as before, only in a more condensed form, each

tion is 31 38 Cal, and for the heat of solution of the anhydrous sulphate he found 0 46 Cal¹. For the heat of solution of the decahydrate Thomsen² gives -18 8 Cal, and Berthelot³ -18 1 Cal. The heat of hydration of the anhydrous salt to the decahydrate is given by Thomsen² as 19 22 Cal, and by Berthelot³ as 18 64 Cal.

* The solubility of the anhydrous salt diminishes with rise of temperature from 33° to 120° C, as indicated in the table of solubility.

Solubility of Sodium Sulphate

Solid Phase, Na₂SO₄.10H₂O

Temperature, °C	0	10	20	30	32 75
Grams Na ₂ SO ₄ in 100 grams water	5 0	9 0	19 4	40 8	50-65

Solid Phase, Na₂SO₄.7H₂O

Temperature, °C	0	5	10	15	20	25
Grams Na ₂ SO ₄ in 100 grams water	19 5	24	30	37	44	53

Solid Phase, Na₂SO₄

Temperature °C	33	35	40	50	60	80	100
Grams Na ₂ SO ₄ in 100 grams water	50 6	50 2	48 8	46 7	45 3	43 7	42 5

Temperature, °C	120	140	160	230
Grams Na ₂ SO ₄ in 100 grams water	41 95	42	44 25	46 4

Lowel⁴ gives the transition-point of the heptahydrate into the anhydrous salt (*E*) as 24 4° C, and that of the decahydrate into the anhydrous salt (*F*) is given by Richards and Wells⁵ as 32 383° C, and by Dickinson and Mueller⁶ as 32 384° C. The solubility relations are graphically represented in fig. 9 (p. 120).

A saturated solution of sodium sulphate containing 42 2 grams of sulphate per 100 grams of water boils at 101 9° C at 751 mm pressure,⁷ or 108 668° C at 760 mm pressure⁸.

Sodium sulphate readily forms a supersaturated solution in water⁹. When a solution is cooled to about 5° C, the heptahydrate crystallizes out. The crystals of the decahydrate weather in air, owing to loss of water of crystallization.

Reduction of sodium sulphate with charcoal at red heat produces sodium sulphide and carbon monoxide, along with sodium polysulphides and carbon dioxide. Addition of alcohol to a solution of sodium sulphate in aqueous hydrogen peroxide precipitates a complex derivative of the formula Na₂SO₄.9H₂O.H₂O₂¹⁰.

¹ Thomsen, *J. prakt. Chem.* 1878 [2] 17 175 compare Pickering, *Trans. Chem. Soc.*, 1884 45 686; Berthelot and Illosvay, *Ann. Chim. Phys.* 1883 [5] 29, 336

Thomsen, *loc. cit.*

² Berthelot, *Ann. Chim. Phys.* 1875, [5] 4 106

³ Lowel, *ibid.* 1857 [3] 49 50

Richards and Wells, *Zeitsch. physikal. Chem.* 1903 43 471

⁴ Dickinson and Mueller, *J. Amer. Chem. Soc.* 1907 29 1318

⁵ Fall of Berkeley, *Phil. Trans.* 1904 [A] 203 209

⁶ Earl of Berkeley and Appleby, *Proc. Roy. Soc.* 1911 [A], 85 459

⁷ Compare Ostwald, *Principles of Inorganic Chemistry* (Macmillan 1904) 492

¹⁰ Tanatar, *Zeitsch. anorg. Chem.*, 1901, 28 255

this reduces the specific gravity of ice 2 per cent or makes it 92, which agrees exact with observation. Hence the 1st fact is explained

The angle of a rhombus is 60° , and its supplement 120° , if any particular angles are manifested in the act of congelation, therefore we ought to expect these, agreeable to the 2d and 3d phenomena

Whenever any remarkable change in the internal constitution of any body takes place whether by the accession and junction of new particles, or by new arrangements of those already existing in it, some modification of the atmospheres of heat must evidently be required, though it may be difficult to estimate the quantity, and sometimes even the kind of change so produced, as in the present case. So far therefore the theory proposed agrees with the 4th phenomenon

In order to explain the other phenomena, will be requisite to consider more particularly the mode by which bodies are expanded by heat—Is the expansion occasioned simply by the enlargement of the individual atmospheres of the component particles? This is the case with elastic fluids, and perhaps with solids but certainly not with liquids. How is it possible that water should be expanded a portion

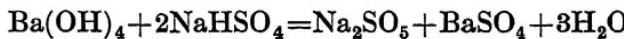
solution in sulphuric acid. At ordinary temperature monoclinic crystals of the monohydrate are deposited, at 50° C triclinic crystals of the anhydrous substance¹

Sodium hydrogen sulphate is a white salt, of density² 2.435 at 13° C Its heat of formation from the elements is given by Thomsen³ as 267.4 Cal, and by Berthelot⁴ as 269.1 Cal, from sulphuric acid and sodium hydroxide it is 14.75 Cal. The heat of solution is given by Thomsen⁵ as 1.19 Cal, but by Berthelot as -0.8 Cal

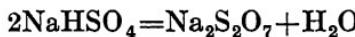
Other investigations concern the molecular volume⁶, and such properties of the solution as viscosity,⁷ density,⁸ and electric conductivity⁹.

Various sulphates of sodium and hydrogen have been prepared. With absolute sulphuric acid sodium sulphate reacts, forming a complex crystalline derivative¹⁰ melting at 40° C, and having the formula Na₂SO₄.8H₂SO₄. d'Ans¹¹ has prepared another example with the composition Na₂SO₄.NaHSO₄. Kendall and Landon¹² have described 2Na₂SO₄.9H₂SO₄, an unstable substance at its melting-point, 60° C (by extrapolation), Na₂SO₄.2H₂SO₄, unstable at its melting-point, and Na₂SO₄.H₂SO₄, melting at 186° C. Other compounds of similar type have been prepared¹³.

Sodium monopersulphate, Na₂SO₅.—This salt is produced by the interaction of barium perhydroxide and sodium hydrogen sulphate¹⁴



Sodium pyrosulphate, Na₂S₂O₇.—The pyrosulphate is produced by the action of sulphur dioxide on sodium sulphate, or by heating the primary sulphate



On ignition, it yields the normal sulphate and sulphur trioxide

Sodium persulphate, Na₂S₂O₈.—The persulphate is formed in solution by the electrolysis of a concentrated aqueous solution of sodium sulphate at low temperature and high current-density. The solid persulphate can be obtained by double decomposition of ammonium persulphate and sodium carbonate either in the solid state or in concentrated solution, the crystalline salt being isolated from the solution either by addition of alcohol or by concentration at reduced pressure¹⁵. When dry and protected from sunlight, it keeps almost unchanged for years¹⁶.

¹ Maignac *Compt rend*, 1857 45 650
Spring *Bull Acad roy Belg* 1904, 290

³ Thomsen, *Thermochemische Untersuchungen I* (1882-1883) 3 233

⁴ Berthelot *Ann Chim Phys* 1875 [5] 4 106
Thomsen *Thermochemistry* (Longmans, 1908) 49 328

⁶ Spring *Bull Acad roy Belg* 1904, 290

⁷ Moore *Physical Rev* 1896 3 321

⁸ Maignac *Annalen Suppl* 1872 8 335

⁹ Buth *Zeitsch physikal Chem* 1892 9 185

¹⁰ Bergius *Zeitsch physikal Chem* 1910 72 338

¹¹ d'Ans *Ber* 1906 39 1534

¹ Kendall and Landon *J Amer Chem Soc* 1920 42 2131

¹³ Compare d'Ans, *Zeitsch anorg Chem* 1913 80, 295 Footh *J Ind Eng Chem* 1919 11, 629

¹⁴ Merck German Patent 1909 No 213457 compare Willstätter and Hauenstein, *Ber* 1909 42 1839

¹⁵ Lowenherz German Patents Nos 77340 and 81404

¹⁶ Elbs and Neher, *Chem Zeit* 1921, 45 1113

in moment, and a portion of ice formed ; heat is then given out which retards the subsequent formation, till at last the whole is congealed. This is the ordinary process of congelation. But if the mass of water cooled is kept in a state of perfect tranquillity, the gradual approach to the rhomboidal form can be carried much farther , the expansion goes on according to the usual manner, and the slight friction or adhesion of the particles is sufficient to counteract the balance of energies in favour of the new formation, till some accidental tremor contributes to adjust the equilibrium A similar operation is performed when we lay a piece of iron on a table, and hold a magnet gradually nearer and nearer , the proximity of the approach, without contact, is much assisted by guarding against any tremulous motion of the table Hence the rest of the phenomena are accounted for

For the density of the anhydrous salt Gerlach¹ gives 1 667 at mean temperature compared with water at 4° C, for the pentahydrate Kopp² gives 1 736, Dewar³ 1 729 at 17° C and 1 7635 at the temperature of liquid air. For the specific heat of the anhydrous salt between 25° and 100° C Pape⁴ gives 0 221, for the pentahydrate between 11° and 44° C Trentinaglia⁵ 0 4447, and for the liquid between 13° and 98° C, 0 569. The molecular heat⁶ of the anhydrous salt is 34 91, and of the pentahydrate 86 22. Berthelot gives the heat of formation of the anhydrous salt from its elements as 256 3 Cal⁷ or 262 6 Cal,⁸ and Thomsen⁹ that of the pentahydrate as 265 07 Cal. Berthelot found for the heat of solution of the anhydrous salt 1 7 Cal at 15° C, his value for that of the pentahydrate at 11° C is -10 8 Cal, and Thomsen's¹⁰ -11 37 Cal, so that the heat of hydration of the anhydrous salt to pentahydrate is about 13 Cal.

Nine hydrates, including thirteen crystalline forms, have been described¹¹. The pentahydrate melts at 48 45° C, and the dihydrate¹² at 50 3° C. Each exists in two isomeric forms. According to Muller,¹³ the unstable form of the pentahydrate crystallizes at -20° C and melts at 38° C, the stable modification crystallizes at -40° C and melts at 48° C. The transition point of the pentahydrate to the dihydrate is 48 17° C, and of the dihydrate to the anhydrous salt 68 5° C. The solubility of the pentahydrate, the dihydrate, and the anhydrous salt, expressed in grams of Na₂S₂O₃ per 100 grams of solution, are given in the table¹⁴.

Temperature °C	0	5	10	15	20	25	30	35	40	45
Pentahydrate	33 4	35 3	37 4	39 1	41 2	43 2	45 2	47 7	50 8	55 3
Dihydrate	52 7	53 4	53 9	54 6	55 2	56 0	57 1	58 2	59 4	60 7
Temperature, °C	40	45	50	55	60	65	70	75	80	
Dihydrate	59 4	60 7	62 3	63 9	65 7	68 0				
Anhydrous salt	67 4	67 6	67 8	68 2	68 5	68 8	69 1	69 4	69 9	

In contact with the solid the saturated solution boils at 126° C, and contains 348 grams of the anhydrous salt in 100 grams of water¹⁵.

Concentrated solutions of sodium thiosulphate are moderately stable, but in dilute solution atmospheric carbon dioxide tends to liberate the unstable thiosulphuric acid, a substance readily changed

¹ Gerlach *Chem Industr* 1886 9 241

Kopp *Annalen* 1855 93 129

³ Dewar *Chem News* 1902 85 277

⁴ Pape *Pogg Annalen* 1865 125 513

⁵ Trentinaglia *Sitzungsber K Akad Wiss Wien* 1876, [2] 72 669

⁶ Schottky, *Physikal Zeitsch* 1909, 10, 634

⁷ Berthelot *Thermochimie* Paris, 1897 1 207

⁸ Berthelot, *Ann Chim Phys* 1879 [5] 17 468

⁹ Ihmsen, *Thermochemistry* (Longmans 1908) 328

¹⁰ Thomsen *ibid* 49

¹¹ Young Mitchell and Burke, *J Amer Chem Soc* 1904 26 1389 1413 1906 28, 315

¹² Gernez *Compt rend* 1909 149, 77

¹³ Muller *Zeitsch physikal Chem* 1914 86 177

¹⁴ Young Mitchell and Burke *loc cit* Taylor, *Proc Roy Soc Edin* 1897-98

²², 249

¹⁵ Gerlach, *Zeitsch anal Chem*, 1887, 26 413

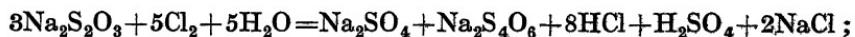
properly called in that view, *attraction of cohesion*, but as it collects them from a dispersed state (as from steam into water) it is called, *attraction of aggregation*, or more simply, *affinity*. Whatever names it may go by, they still signify one and the same power. It is not my design to call in question this conclusion, which appears completely satisfactory, but to shew that we have hitherto made no use of it, and that the consequence of the neglect, has been a very obscure view of chemical agency, which is daily growing more so in proportion to the new lights attempted to be thrown upon it

The opinions I more particularly allude to, are those of Berthollet on the Laws of chemical affinity, such as that chemical agency is proportional to the mass, and that in all chemical unions, there exist insensible gradations in the proportions of the constituent principles. The inconsistence of these opinions, both with reason and observation, cannot, I think, fail to strike every one who takes a proper view of the phenomena.

Whether the ultimate particles of a body, such as water, are all alike, that is, of the same figure, weight, &c is a question of some importance. From what is known, we have no reason to apprehend a diversity in these

oxidized directly to sulphate without the intermediate formation of tetra thionate, weak alkali having a similar, though only partial, effect

The action of hypochlorite solutions on sodium thiosulphate is in accordance with the equations¹



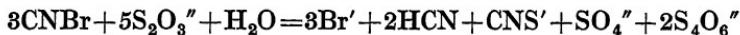
or



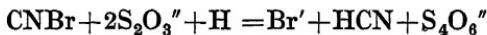
In presence of acids or sodium hydrogen carbonate, the reaction accords with the equation



Kurtenacker² found that cyanogen bromide and iodide react with sodium thiosulphate in neutral solution in accordance with the equation



In acidic solution the thiosulphate is converted into tetrathionate



The reaction in neutral solution probably involves two stages, the solution becoming temporarily alkaline through the formation of sodium cyanide, which reacts with the generated tetrathionate in accordance with the equation



The thiosulphate produced then reacts with the halogen cyanide

A mixture of crystallized sodium thiosulphate and ammonium nitrate finds application as a freezing-mixture³

References are appended to investigation of the refractivity⁴ of the solid, to properties of solutions such as the transition-points of the hydrates,⁵ supersaturation,⁶ electric conductivity,⁷ density,⁸ vapour pressure,⁹ boiling point,¹⁰ molecular depression of the freezing-point¹¹ refractivity,¹² solubility in alcohol,¹³ and electrolysis¹⁴, and to the formation of mixed thiosulphates of sodium and potassium and their isomerism¹⁵

¹ Diénert and Wandenbulcke *Compt rend* 1919 **169** 29

² Kurtenacker *Zeitsch anorg Chem* 1921 **116** 243 compare however Meineke *ibid* 1893 **2**, 157 Dixon and Taylor *Trans Chem Soc* 1913 **103** 974

³ Schubardt *German Patent* 1911 No 233596

⁴ Dufet *Bull Soc franç Min* 1888 **11** 123 191

⁵ Trentinaghia *Sitzungsber K Akad Wiss Wien* 1876 [2] **72** 669 Richards and Churchill *Zeitsch physikal Chem* 1899 **28** 314 Dawson and Jackson *Trans Chem Soc* 1908 **93** 344, Guthrie *Phil Mag* 1878 [5] **6** 41

⁶ Blumcke *Zeitsch physikal Chem* 1896 **20** 586

⁷ Kuster and Thiel *Zeitsch anorg Chem*, 1899 **21** 401

⁸ Damien *Ann École Norm* 1881 [2] **10** 233

⁹ Tammann *Mem Acad St Petersbourg* 1887, [7] **35** No 9 compare Leesaur *Ann Chem Phys* 1896 [7] **9** 537

¹⁰ Gerlach *Zeitsch anal Chem* 1887 **26** 413

¹¹ Richards and Faber *Amer Chem J* 1899 **21** 172 compare Filtor *Pharm Post* 1902 **34** 769

¹² Bary *Compt rend* 1892 **114** 827, compare Miers and Isaac *Trans Chem Soc* 1906 **89** 413

¹³ Parmentier *Compt rend* 1896, **122** 135 compare Bruner *ibid* 1895 **121** 59

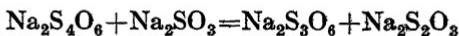
¹⁴ Thatcher, *Zeitsch physikal Chem* 1904 **47** 641

¹⁵ Schwicker *Ber* 1889, **22**, 1730

actual contact. This appears to be satisfactorily proved by the observation, that the bulk of a body may be diminished by abstracting some of its heat. But from what has been stated in the last section, it should seem that enlargement and diminution of bulk depend perhaps more on the arrangement, than on the size of the ultimate particles. Be this as it may, we cannot avoid inferring from the preceding doctrine on heat, and particularly from the section on the natural zero of temperature, that solid bodies, such as ice, contain a large portion, perhaps $\frac{1}{3}$ of the heat which the same are found to contain in an elastic state, as steam.

We are now to consider how these two great antagonist powers of attraction and repulsion are adjusted, so as to allow of the three different states of *elastic fluids*, *liquids*, and *solids*. We shall divide the subject into four Sections, namely, first, *on the constitution of pure elastic fluids*, second, *on the constitution of mixed elastic fluids*, third, *on the constitution of liquids*, and fourth, *on the constitution of solids*.

The tetrathionate is converted by the action of sodium sulphite into trithionate and thiosulphate ¹

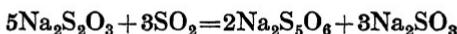


With alkali-metal cyanides the tetrathionate reacts in accordance with the equation ²

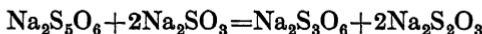


At the boiling-point, in presence of excess of cyanide, the thiosulphate formed reacts further to produce thiocyanate and sulphite

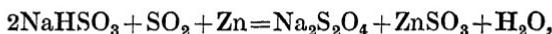
Sodium pentathionate, $\text{Na}_2\text{S}_5\text{O}_6$ —This salt has not been obtained in the pure state, but is said to be one of the products of the decomposition of acid solutions of sodium thiosulphate, the sulphur dioxide liberated reacting with the thiosulphate ³



It is also said to react with sodium sulphite, yielding the trithionate and thiosulphate ³



Sodium hyposulphite, $\text{Na}_2\text{S}_2\text{O}_4$ —The hyposulphite was first prepared in solution by Schutzenberger ⁴ by reducing a solution of sodium hydrogen sulphite with zinc, but the yield is unsatisfactory. Bernthsen and Bazlen ⁵ obtained the pure substance by reducing the primary sulphite with zinc dust in presence of sulphurous acid,



precipitating the zinc and removing the excess of acid by addition of milk of lime, the hyposulphite being salted out in the form of dihydrate by addition of sodium chloride. They recommend increasing the stability of the dihydrate by washing with acetone, at first dilute and finally pure, and drying in a vacuum. Jellinek ⁶ advises heating the dihydrate at 60° C in vacuum, the process transforming it into the stable anhydrous salt. The hyposulphite can also be produced under special experimental conditions ⁷ by the electrolytic reduction of sodium hydrogen sulphite, Jellinek ⁸ having obtained a 7 to 8 per cent solution by this means. Prepared by this process, it finds application in the reduction of indigo to indigo-white ⁹.

¹ Rasching *Zeitsch angew Chem* 1920 33 260

Kertenacker and Hentsch *Zeitsch anorg Chem* 1921 117 202 compare Gutmann *Ber*, 1906 39 509 McKenzie and Marshall *Trans Chem Soc* 1908 93 1726

² Rasching *Zeitsch angew Chem* 1920 33 260

⁴ rend 1869 69 196 1872, 75 879

⁵ Ber 1900 33 126 Bazlen *Ber* 1905 38, 1057

⁶ Kain Jellinek *Zeitsch anorg Chem* 1911 70 93

⁷ Frank *Zeitsch Elektrochem* 1904 10 450 Chaumat German Patent, 1910 No 221614 Elbs and Becker, *Zeitsch Elektrochem* 1904 10 361 Julius Meyer *Zeitsch anorg Chem* 1903 34 43

⁸ Karl Jellinek and E Jellinek *Zeitsch physikal Chem* 1919 93, 325

⁹ Hochster Farbwurke German Patent, 1902 No 139567

of elastic fluid is found to expand whenever the pressure is taken off This proves that the repulsion exceeds the attraction in such case The absolute attraction and repulsion of the particles of an elastic fluid, we have no means of estimating, though we can have little doubt but that the cotemporary energy of both is great, but the excess of the repulsive energy above the attractive can be estimated, and the law of increase and diminution be ascertained in many cases Thus in steam, the density may be taken at $\frac{1}{1728}$ that of water, consequently each particle of steam has 12 times the diameter that one of water has, and must press upon 144 particles of a watery surface, but the pressure upon each is equivalent to that of a column of water of 34 feet, therefore the excess of the elastic force in a particle of steam is equal to the weight of a column of particles of water, whose height is $34 \times 144 = 4896$ feet And further, this elastic force decreases as the distance of the par icles increases With respect to steam and other elstic fluids then, the force of cohesion is entirely counteracted by that of repulsion, and the only force which is efficacious to move the particles is the excess of the repulsion above the attraction Thus, if the attraction be as 10 and the repulsion as 12, the effective repulsive force is as 2 It

sulphate, a reaction applied by Bazlen and Bernthsen to the quantitative estimation of the salt¹



The action of selenium and tellurium on sodium hyposulphite has been investigated by Tschugaev and Chlopin²

The hyposulphite was employed by Julius Meyer³ in the preparation of metallic colloidal solutions. It finds technical application as a reducer in the dye-industry. When administered intravenously, it exerts a toxic effect⁴

Sodium selenides—The monoselenide, Na_2Se , is formed by the action of selenium on a solution of excess of sodium in liquid ammonia, and separates out⁵. It can also be produced by the interaction of selenium and sodium hyposulphite, $\text{Na}_2\text{S}_2\text{O}_4$ ⁶. It melts above 875° C, and on exposure to air its solution in water acquires a reddish colour, and deposits selenium. In solution it is extensively hydrolyzed, and under these conditions may be regarded as a mixture of sodium hydrogen selenide, NaSeH , and sodium hydroxide. Four hydrates are known, with 4½, 9, 10, and 16 molecules of water respectively⁷. For the heat of formation of the anhydrous compound Fabre⁸ gives 59.7 Cal, and for the heat of solution at 14° C, 18.6 Cal. He has also investigated the heat of solution of the hydrates

When excess of selenium reacts with a solution of sodium in liquid ammonia, sodium tetraselenide, Na_2Se_4 , separates⁹. By fusion of sodium with selenium, Mathewson¹⁰ has isolated between 500° and 250° C the diselenide Na_2Se_2 , triselenide Na_2Se_3 , tetraselenide Na_2Se_4 , and hexaselenide Na_2Se_6 . They are dark grey substances, unstable in air, and readily soluble in water to red solutions

Sodium selenite, Na_2SeO_3 —The selenite is formed by heating a mixture of selenious acid and sodium chloride¹¹. At ordinary temperature the aqueous solution deposits the pentahydrate, above 60° C the anhydrous salt¹². For the heat of formation from its elements in aqueous solution Thomsen gives 238.4 Cal

Berzelius mentions a salt which was either sodium hydrogen selenite, NaHSeO_3 , or pyro selenite, $\text{Na}_2\text{Se}_2\text{O}_5$.

Sodium selenate, Na_2SeO_4 —The selenate is prepared from sodium selenite by electrolytic oxidation with platinum electrodes at ordinary temperature¹³. A by-product analogous to the dithionite obtained in the electrolytic oxidation of sodium sulphite is not formed¹⁴

¹ Bazlen and Bernthsen *Ber*, 1910 43, 501

Tschugaev and Chlopin *Ber* 1914 47, 1269

² Julius Meyer *Zeitsch anorg Chem* 1903, 34, 43

³ Heyl and Greer *Amer J Pharm* 1922 94, 50

⁴ Hugot *Compt rend*, 1899 129, 299

⁵ Tschugaev and Chlopin *loc cit*

⁶ Fabre *Ann Chim Phys* 1887 [6] 10, 505 Clever and Muthmann *Zeitsch anorg Chem* 1895 10, 17

⁷ Fabre *Ann Chim Phys* 1887 [6] 10, 505

⁸ Hugot *Compt rend* 1899 129, 299

¹⁰ Mathewson *J Amer Chem Soc* 1907 29, 867

¹¹ Cameron and McCallan *Chem News* 1889 59, 258

¹² Nilson *Bull Soc chim* 1874 [2] 21, 253

¹³ Muller *Ber* 1903 36, 4262

¹⁴ Compare Forster and Friessner *Ber* 1902 35, 2515

the density of the atmospheres of heat must fluctuate with the pressure. Thus, suppose a measure of air were expanded into 8 measures, then, because the diameters of the elastic particles are as the cube root of the space, the distances of the particles would be twice as great as before, and the elastic atmospheres would occupy nearly 8 times the space they did before, with nearly the same quantity of heat whence we see that these atmospheres must be diminished in density in nearly the same ratio as the mass of elastic fluid

Some elastic fluids, as hydrogen, oxygen, &c resist any pressure that has yet been applied to them In such then it is evident the repulsive force of heat is more than a match for the affinity of the particles, and the external pressure united To what extent this would continue we cannot say, but from analogy we might apprehend that a still greater pressure would succeed in giving the attractive force the superiority, when the elastic fluid would become a liquid or solid In other elastic fluids, as steam, upon the application of compression to a certain degree, the elasticity apparently ceases altogether, and the particles collect in small drops of liquid, and fall down. This phenomenon requires explanation

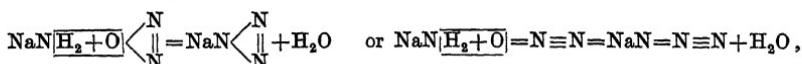
From the very abrupt transition of steam

Sodium tellurate,¹ $\text{Na}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ —The tellurate is prepared in a similar manner to the selenate.² It is not readily soluble, and undergoes reduction easily to tellurium.³ It is only known in the form of dihydrate.

Sodium chromates —An account is given in this series, Vol. VII, of the modes of preparation and of the properties of sodium chromate and dichromate.

Sodium nitride, Na_3N —The nitride is formed by submitting sodium to the action of the silent electric discharge in an atmosphere of nitrogen.⁴ It is decomposed by water, with energetic evolution of ammonia. Fischer and Schröter⁵ also claim to have prepared it, but they give no analyses or formula.

Sodium hydrazoate, NaN_3 —The hydrazoate is formed by neutralizing hydrazoic acid with sodium hydroxide,⁶ by the interaction of sodamide and nitrous oxide.⁷



and by decomposing hydrazoyl chloride with sodium hydroxide.⁸



Sodium hydrazoate forms colourless crystals, which melt without decomposition, but explode at a temperature higher than the melting-point. At 10°C 100 grams of water dissolve 40.16 grams, at 17°C 41.7 grams.

Sodamide, NaNH_2 —Sodamide is formed by the action of liquid ammonia on the metal,⁹ or by passing dry ammonia over fused sodium¹⁰ or one of its alloys.¹¹ An apparatus for its preparation has been described by Wöhler and Stang-Lund.¹²

Sodamide is a white substance. According to Wöhler and Stang Lund,¹² it melts at 210°C , and not between 149° and 155°C , as stated by Titherley¹³, but McGee¹⁴ found that it melts sharply at 208°C . He was unable to prepare the blue solutions of sodium in the amide described by Titherley,¹⁵ and found no solvent action on glass below 240°C . Contact of the amide with glass for several days at 270°

¹ On sodium tellurate compare Lenher and Wolessensky, *J Amer Chem Soc* 1913, 35, 718.

² Funk *Ber* 1900 33 3696.

³ Muller *Ber* 1903 36 4262.

⁴ Zehnder *Wied Annalen*, 1894 52 56.

⁵ Fischer and Schröter *Ber*, 1910 43 1465.

⁶ Dennis and Benedict *Zeitsch anorg Chem* 1898 17 19.

⁷ Wislicenus *Ber* 1892, 25 2084. Curtius *Ber* 1890 23 3023. 1891 24 3341. Curtius and Russom *J prakt Chem* 1898 [2] 58 278.

⁸ Raschig *Ber* 1908 41 4194.

⁹ Compare Joannis *Compt rend* 1887 109 900. 1891 112 392. 1892 115 820. *Ann Chim Phys* 1906 [8] 7 5. Ruff and Giesel *Ber* 1906 39, 828.

¹⁰ Gay Lussac and Thenard, *Recherches Physico Chimiques*, Paris 1811 1 354. Titherley *Trans Chem Soc*, 1894 65 504. de Forcrand *Compt rend* 1895 121, 66.

¹¹ Gold und Silber Scheideanstalt vormals Rössler German Patent 1901 No 117623.

¹² Wöhler and Stang Lund *Zeitsch Elektrochem* 1918 24 261.

¹³ Titherley *Trans Chem Soc* 1894 65 504.

¹⁴ McGee *J Amer Chem Soc* 1921 43 586.

¹⁵ Titherley *loc cit*.

The constitution of a liquid, as water, must then be conceived to be that of an aggregate of particles, exercising in a most powerful manner the forces of attraction and repulsion, but nearly in an equal degree.—Of this more in the sequel

SECTION 2.

ON THE CONSTITUTION OF MIXED ELASTIC FLUIDS

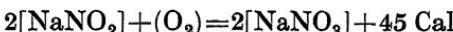
When two or more elastic fluids, whose particles do not unite chemically upon mixture, are brought together, one measure of each, they occupy the space of two measures, but become uniformly diffused through each other, and remain so, whatever may be their specific gravities. The fact admits of no doubt, but explanations have been given in various ways, and none of them completely satisfactory. As the subject is one of primary importance in forming a system of chemical principles, we must enter somewhat more fully into the discussion.

Dr Priestley was one of the earliest to notice the fact it naturally struck him with surprise,

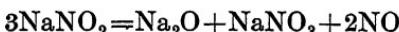
reduction of the nitrate¹, the action of nitrous fumes containing excess of nitric oxide on a solution of sodium hydroxide or carbonate², and the action of oxygen on ammonia in presence of platinized asbestos as catalyst, the ammonium nitrite produced being transformed by treatment with sodium hydroxide, and the evolved ammonia being available for further oxidation³

Sodium nitrite is a white, crystalline salt. Its melting-point is given by Divers² as 213° C, but by Matignon and Marchal⁴ as 276.9° C (corr.), and by Bruni and Meneghini⁵ as 284° C. At 15° C 100 grams of water dissolve 88.3 grams. The heat of solution is -3.52 Cal, and the heat of formation in solution from the elements is 88.52 Cal⁴.

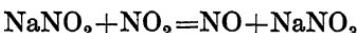
In aqueous solution at 100° C and between 50 and 55 atmospheres of pressure, sodium nitrite is not oxidized by prolonged contact with oxygen, even in presence of a catalyst⁴. When heated in an atmosphere of oxygen for nine hours at 175 atmospheres of pressure, the temperature being gradually raised from 395° to 530° C, the solid is almost completely oxidized to sodium nitrate, but the reaction is too slow for practical application⁶.



When heated, sodium nitrite decomposes in accordance with the equation⁷



Heating in an atmosphere of nitrogen peroxide yields nitric oxide and sodium nitrate⁷



At 60° C in an atmosphere of carbon dioxide free from air, a 5 per cent solution of sodium nitrite is decomposed by metallic copper, with evolution of nitrous fumes, but there is not sufficient evidence to enable the course of the reaction to be indicated by means of an equation⁸.

When an anolyte of sodium nitrite dissolved in twice its weight of water is electrolyzed with a silver anode, a complex salt of the formula $\text{NaAg}(\text{NO}_2)_2$ is formed at the anode. On evaporation of the solution over sulphuric acid *in vacuo*, it separates in bright yellow crystals⁹.

The nitrite finds extensive application in the manufacture of certain synthetic dyestuffs.

References are appended to the solubility in alcohol,¹⁰ and such properties of the aqueous solution as density,¹¹ vapour pressure,¹² and electric conductivity¹³.

¹ Forster, *Elektrochemie wasseriger Lösungen* Leipzig 1905 325

² Divers *Trans Chem Soc* 1899 75 85 87 95

³ Warren *Chem News*, 1891 63 290

⁴ Matignon and Marchal *Compt rend*, 1920 170 232

Bruni and Meneghini *Zeitsch anorg Chem* 1909 64, 193

⁶ Matignon and Monnet *Compt rend* 1920 170 180

⁷ Oswald, *Ann Chim Phys* 1914 [9] 1 32

⁸ Peters *Zeitsch anorg Chem* 1919 107 313

⁹ Jeffery *Trans Faraday Soc* 1920 15 16

¹⁰ Lobry de Bruyn *Rcc trav chim* 1892 11 156

¹¹ Boguski *Bull Acad Sci Cracow* 1898 123

¹² Tammann *Mem Acad St Petersbourg* 1887 [7] 35 No 9

¹³ Schumann *Ber* 1900 33 532. Rocard and Nicmentowsky *Zeitsch physikal Chem* 1897 22 147, compare Holborn, Landolt, Bornstein, and Meyerhoffer's *Tabellen*

3rd ed., Berlin 1905, 749

probable that the notion of water being dissolved in air, led to that of air being dissolved in air—Philosophers found that water gradually disappeared or evaporated in air, and increased its elasticity, but steam at a low temperature was known to be unable to overcome the resistance of the air, therefore the agency of affinity was necessary to account for the effect In the permanently elastic fluids indeed, this agency did not seem to be so much wanted, as they are all able to support themselves, but the diffusion through each other was a circumstance which did not admit of an easy solution any other way In regard to the solution of water in air, it was natural to suppose, nay, one might almost have been satisfied without the aid of experiment, that the different gases would have had different affinities for water, and that the quantities of water dissolved in like circumstances, would have varied according to the nature of the gas Saussure found however that there was no difference in this respect in the solvent powers of carbonic acid, hydrogen gas, and common air—It might be expected that at least the *density* of the gas would have some influence upon its solvent powers, that air of half density would take half the water, or the quantity of water would diminish in some proportion to

Schuller¹ found 0 2650, Regnault² for the previously fused salt 0 2782, and Person³ for the liquid between 320° and 480° C 0 41 The latent heat of fusion for 1 gram-molecule at 310 5° C is given by Person³ as 5 5 Cal The heat of formation from the elements is stated by Thomsen⁴ to be 111 25 Cal , and by Berthelot⁵ to be 110 7 Cal , that from nitric acid and sodium hydroxide is given by Thomsen⁶ as 18 68 Cal , and by Berthelot as 18 5 Cal For the heat of solution Thomsen⁷ gives -5 0 Cal , and Berthelot⁸ between 10° and 15° C -4 7 Cal The heptahydrate⁹ melts at -15 7° C

The table summarizes the results obtained by the Earl of Berkeley¹⁰ in his work on the solubility of sodium nitrate

Temperature, °C	Grams of NaNO ₃ in 100 grams of Water	Temperature, °C	Grams of NaNO ₃ in 100 grams of Water
0	73	60	124 6
10	80 5	70	136
20	88	80	148
30	96 2	90	161
40	104 9	100	175 5
50	114	119	208 8

Gerlach¹¹ gives the boiling-point of the saturated solution in contact with the solid as 120° C , and its strength as 222 grams per 100 grams of water , the Earl of Berkeley and Applebey's¹² value for the boiling point is 120 20° C at 760 mm

In the fused state sodium nitrate is dissociated to the extent of 61 7 per cent , and its mean molecular refraction between 320° and 440° C is 11 54¹³

The molecular electric conductivity of sodium nitrate between 321 5° and 487 3° C is given by the formula¹⁴

$$\mu_t = 41 56 + 0 205(t - 300)$$

Sodium nitrate is a very deliquescent substance,¹⁵ and is therefore unsuited for the manufacture of explosives It is employed in agriculture as a fertilizer, and by double decomposition with potassium chloride yields potassium nitrate Large quantities are reduced to

¹ Schuller, *Pogg Annalen* 1869 136 70 235

² Regnault, *ibid* 1841 53 60 243

³ Person *Ann Chim Phys*, 1847, [3] 21 295

⁴ Thomsen, *Thermochemistry* (Longmans 1908) 324, 325

⁵ Berthelot *Ann Chim Phys* 1873, [4] 30 440

⁶ Thomsen *Thermochemistry* (Longmans 1908) 115

⁷ Thomsen, *J prakt Chem* 1878 [2] 17, 175

⁸ Berthelot *Ann Chim Phys*, 1875, [5] 4, 521

⁹ Ditte *Compt rend* 1875 80 1164

¹⁰ Earl of Berkeley *Phil Trans*, 1904, [A] 203 209

¹¹ Gerlach *Zeitsch anal Chem* 1887, 26 413

¹² Earl of Berkeley and Applebey *Proc Roy Soc*, 1911 [A], 85, 489

¹³ G Meyer and Heck, *Zeitsch Elektrochem*, 1922, 28 21

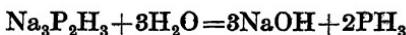
¹⁴ Jaeger and Kapma *Zeitsch anorg Chem*, 1920, 113 27

¹⁵ Compare Kortwright, *J Physical Chem* 1899 3 328

experiments upon which a series of essays were founded, which were read before the Literary and Philosophical Society of Manchester, and published in the 5th Vol of their memoirs, 1802

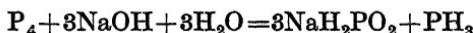
The distinguishing feature of the new theory was, that the particles of one gas are not elastic or repulsive in regard to the particles of another gas, but only to the particles of their own kind. Consequently when a vessel contains a mixture of two such elastic fluids, each acts independently upon the vessel, with its proper elasticity, just as if the other were absent, whilst no mutual action between the fluids themselves is observed. This position most effectually provided for the existence of vapour of any temperature in the atmosphere, because it could have nothing but its own weight to support, and it was perfectly obvious why neither more nor less vapour could exist in air of extreme moisture, than in a vacuum of the same temperature. So far then the great object of the theory was attained. The law of the condensation of vapour in the atmosphere by cold, was evidently the same on this scheme, as that of the condensation of pure steam, and experience was found to confirm the conclusion at all temperatures. The only thing now wanting to completely establish

At low temperatures ammonia reacts with sodium and red phosphorus to form a reddish-brown, amorphous mass, considered by Hugot¹ to be sodium phosphide. With excess of sodium, yellow crystals of the formula $\text{Na}_3\text{P}_2\text{H}_3$ are formed. They react with water and acids, evolving phosphine.



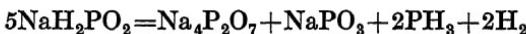
Sodium dihydrophosphide, NaPH_2 , is a white substance formed by treating a solution of sodium in liquid ammonia with phosphine, and evaporating the ammonia.² *Trisodium phosphide*, Na_3P , is produced simultaneously. The mixture reacts with water, evolving phosphine.

Sodium hypophosphite, NaH_2PO_2 .—The hypophosphite is formed by the interaction of sodium hydroxide and phosphorus.



It can also be obtained by decomposing the calcium or barium salt by the action of sodium carbonate in alcoholic solution.

Sodium hypophosphite is a powerful reducer. On heating it evolves phosphine, the reaction being often so violent as to cause explosion.³



At 21.5°C the heat of formation from sodium hydroxide and the acid is 15.16 Cal ,⁴ and that from the elements in solution is 198.4 Cal .⁵ The electric conductivity has been studied by Arrhenius.⁶

Sodium phosphites.—*Disodium hydrogen phosphite*, $\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$, is obtained by concentration of a solution of phosphorous acid neutralized with sodium carbonate, and over sulphuric acid changes to the anhydrous salt. The pentahydrate is very deliquescent. The anhydrous salt melts at 53°C , and above this temperature is oxidized to sodium phosphate, with evolution of phosphine.⁷ The heat of formation from the elements is 285.1 Cal ,⁸ and from the acid and sodium hydroxide in solution 28.45 Cal .⁹ The heat of hydration of the anhydride to the pentahydrate is 13.7 Cal .

Sodium dihydrogen phosphite, $\text{NaH}_2\text{PO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, crystallizes when a solution of equimolecular proportions of phosphorous acid and sodium hydroxide is cooled to -23°C . The heat of formation of the anhydrous salt from the elements is 388.8 Cal ,⁸ and from the acid and sodium hydroxide in solution 14.83 Cal .¹⁰ The heat of hydration of the hydrate is 6.05 Cal .

When anhydrous sodium dihydrogen phosphite is heated at 160°C it is converted into *disodium dihydrogen pyrophosphate*, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_5$. It forms microscopic crystals, reconverted by heating in solution into the parent substance. The heat of formation from the elements is 599 Cal .¹¹

¹ Hugot *Compt rend* 1895 121 206 1898 126, 1719
Joannis *ibid* 1894 119 557

² Rammelsberg *Sitzungsber K Akad Wiss Berlin* 1872 412

³ Compare Arrhenius *Zeitsch physikal Chem* 1892 9 339
Thomsen *Thermochimische Untersuchungen I* (1882-1883), 1, 421

⁴ Arrhenius *loc cit*

⁵ Amat *Compt rend* 1890 110 191

⁶ Thomsen *Thermochimische Untersuchungen I* (1882-1883) 1, 95

⁷ Thomsen, *Thermochemistry* (Longmans, 1908) 96

¹⁰ Thomsen *ibid*, 98

¹¹ Amat *loc cit*

consequently reprobated. This must have have arisen partly at least from my being too concise, and not sufficiently clear in its exposition

Dr. Thomson was the first, as far as I know, who publicly animadverted upon the theory, this gentleman, so well known for his excellent System of Chemistry, observed in the first edition of that work, that the theory would not account for the equal distribution of gases; but that, granting the supposition of one gas neither attracting nor repelling another, the two must still arrange themselves according to their specific gravity. But the most general objection to it was quite of a different kind, it was admitted, that the theory was adapted so as to obtain the most uniform and permanent diffusion of gases, but it was urged, that as one gas was as a vacuum to another, a measure of any gas being put to a measure of another, the two measures ought to occupy the space of one measure only. Finding that my views on the subject were thus misapprehended, I wrote an illustration of the theory, which was published in the 3d Vol. of Nicholson's Journal, for November, 1802. In that paper I endeavoured to point out the conditions of mixed gases more at large, according to my hypothesis, and particularly touched upon the

crystalline salt, its solubility¹ at 10° C per 100 grams of water being 39 grams, and at 30° C 241 grams

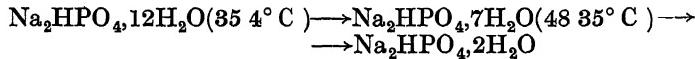
*Solubility of Disodium Hydrogen Orthophosphate (Shiomi)*²

Temperature, °C	10 26	25 15	40 29	60 23	99 77
Grams Na ₂ HPO ₄ in 100 g H ₂ O	3.55	12.02	54.88	88.00	102.15

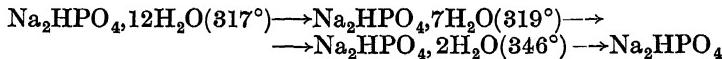
There are three breaks in the curve at 36.45° C, corresponding with the transition from dodecahydrate to heptahydrate, at 48° C (probably heptahydrate to dihydrate), and at 95.2° C (probably dihydrate to anhydrous salt). Later work³ has indicated the dodecahydrate to exist in two forms, α and β , their transition-temperature being 29.6° C. The transition-temperature of the α -hydrate to the heptahydrate was found to be 35.0° C. The solubilities of the two dodecahydrates were also determined.

For the density of the dodecahydrate Clarke⁴ gives 1.535, and at the temperature of liquid air Dewar⁵ gives the value 1.545. For the specific heat of the crystalline salt between -20° and 2° C Person⁶ found 0.454, and for the fused salt between 44° and 97° C 0.758, for the solid dodecahydrate Nernst and Lindemann⁷ give 0.3723, and for the heptahydrate 0.3230. Thomsen⁸ gives 50.04 Cal as the heat of formation of the dihydrate from sodium hydroxide and phosphoric acid.⁹ The latent heat of fusion of the dodecahydrate at 36.1° C is given by Person¹⁰ as 23.9 Cal.

For the transition-points of the dodecahydrate to the heptahydrate and of the heptahydrate to the dihydrate d'Ans and Schreiner¹¹ give



At a pressure of 0.1 atm Blitz¹² gives the transition-points on the absolute scale as



The transition-point of the dodecahydrate into the heptahydrate is given by Person¹³ as 36.4° C, Baur¹⁴ 36.6° C, and Tilden¹⁵ 35.0° C, and the transition-point into the anhydrous salt by Muller¹⁶ as 43.5° C.

¹ Mulder, *Bydragen, etc.*, Rotterdam, 1864, 100, d'Ans and Schreiner, *Zeitsch physikal Chem.*, 1910, 75, 95.

² Shiomi *Mem Coll Sci Eng Kyoto* 1909 I, 406.

³ Hammick, Goadby and Booth, *Trans Chem Soc* 1920, II, 1589.

⁴ Clarke *Constants of Nature*, 2nd ed. Washington 1888 I, 114.

⁵ Dewar, *Chem News*, 1902, 85, 277.

⁶ Person, *Pogg Annalen* 1847, 70, 300.

⁷ Nernst and Lindemann, *Sitzungsber K Akad Wiss Berlin*, 1910, 247.

⁸ Thomsen, *Thermochemische Untersuchungen* Leipzig, 1882-1883, 3, 233.

⁹ Compare Berthelot and Lougounine *Ann Chim Phys* 1876 [5] 9 28.

¹⁰ Person *ibid*, 1849 [3] 27 252, 259.

¹¹ d'Ans and Schreiner *Zeitsch physikal Chem.*, 1910, 75, 95.

¹² Blitz *ibid* 1909, 67 561.

¹³ Person *loc cit*.

¹⁴ Baur *Zeitsch physikal Chem* 1895 I, 18 180.

¹⁵ Tilden, *Trans Chem Soc*, 1884 45, 268.

¹⁶ Muller *J Chim phys*, 1909, 7, 534.

atmosphere, in which he has entered largely into a discussion of the new theory. This celebrated chemist, upon comparing the results of experiments made by De Luc, Saussure, Volta, Lavoisier, Watt, &c. together with those of Gay Lussac, and his own, gives his full assent to the fact, that vapours of every kind increase the elasticity of each species of gas alike, and just as much as the force of the said vapours in vacuo, and not only so, but that the specific gravity of vapour in air and vapour in vacuo is in all cases the same (Vol I Sect 4.) Consequently he adopts the theorem for finding the quantity of vapour which a given volume of air can dissolve, which I have laid down, namely,

$$s = \frac{p}{p-f}$$

where p represents the pressure upon a given volume (1) of dry air, expressed in inches of mercury, f = the force of the vapour in vacuo at the temperature, in inches of mercury, and s = the space which the mixture of air and vapour occupies under the given pressure, p , after saturation. So far therefore we perfectly agree but he objects to the theory by which I attempt to explain these phenomena, and substitutes another of his own.

The first objection I shall notice is one that

The product is a white substance, its melting-point being given by Carnelley¹ as 888° C and by Le Chatelier² as 957° C and also³ as 970° C For the density Schroder⁴ gives 2 534, and Mohr⁵ 2 885 Between 17° and 98° C Regnault⁶ found the specific heat to be 0 2283. The heat of solution is given by Thomsen⁷ as 11 85 Cal

Sodium pyrophosphate crystallizes from water as the monoclinic decahydrate Its density is given by Playfair and Joule⁸ as 1 836, Mohr⁹ 1 773, and Dufet¹⁰ 1 824, and its heat of solution by Thomsen¹¹ as -11 67 Cal At 20° C 100 grams of water dissolve 6 2 grams, and at 80° C 80 grams,¹² yielding a solution of faint alkaline reaction

Other investigations concern the refractivity¹³, and properties of the solution such as density,¹⁴ vapour-pressure,¹⁵ and electric conductivity¹⁶

Disodium dihydrogen pyrophosphate, Na₂H₂P₂O₇.—This substance is formed by heating sodium dihydrogen phosphate at about 200° C



Above 300° C it is converted into sodium metaphosphate

In addition to the anhydrous salt, a tetrahydrate,¹⁷ and also a hexahydrate¹⁸ of density¹⁹ 1 848, are known The aqueous solution has an acidic reaction, and reacts with sodium hydroxide to form the normal pyrophosphate

Sodium metaphosphate, NaPO₃.—The metaphosphate is prepared by the interaction of sodium nitrate and phosphoric acid at 330° C²⁰ It is a white, vitreous mass, almost insoluble in water, and melting²¹ at 617 ± 2° C It is sometimes called "Maddrell's salt," after its discoverer²² The semihydrate, NaPO₃.½H₂O, is formed by heating sodium ammonium hydrogen phosphate at 160° to 170° C, and subsequently raising the temperature to 320° C²³ Tammann²⁴ has proved the existence

¹ Carnelley, *Trans Chem Soc* 1878 33 273

² Le Chatelier, *Bull Soc chim* 1887, [2] 47 300

³ Le Chatelier, *Compt rend* 1894 118 350

⁴ Schroder *Dichtigkeitsmessungen* Heidelberg 1873

⁵ Compare Clarke, *Constants of Nature* 2nd ed, Washington 1888 1 118

⁶ Regnault *Pogg Annalen*, 1841 53 60 243

⁷ Thomsen *J prakt Chem* 1878 [2] 17 175, *Thermochemistry* (Longmans 1908) 49

⁸ Playfair and Joule *Mem Chem Soc* 1843-1845 2 401

⁹ Compare Clarke *loc cit*

¹⁰ Dufet *Bull Soc franq Min* 1887, 10 77

¹¹ Thomsen *loc cit*

¹² Poggiale *J Pharm Chim* 1863 [3] 44 273

¹³ Dufet *loc cit*

¹⁴ Fouque *Ann Observat Paris* 1868 9 172

¹⁵ Tammann *Mem Acad St Petersbourg* 1887 [7] 35 No 9 *Wied Annalen* 188,

²⁴ 530

¹⁶ Walden *Zeitsch physikal Chem*, 1887 1 529

¹⁷ Rammelsberg *Gesamt Abhandl* 1888 127

¹⁸ Beyer *J prakt Chem* 1869 106 501

¹⁹ Dufet *loc cit*

⁰ von Knorre *Zeitsch anorg Chem* 1900 24 378

¹ Carnelley *loc cit*

Maddrell *Phil Mag* 1847 [3] 30 322

²³ Langheld Oppmann and E Meyer *Ber* 1912 45 3753

²⁴ Tammann *J prakt Chem* 1892 [2] 45 421 *Zeitsch physikal Chem* 1890

⁶ 124 compare Warschauer *Zeitsch anorg Chem* 1903 36 188 *Platinum Pogg Annalen* 1849 78 361 Fleitmann and II *Annalen* 1848 65 307 Jawein and Thillot *Ber* 1889 22 655 Clarke *Constants of Nature* 2nd ed, Washington 1888 1 118 Tammann *Mem Acad St Petersbourg* 1887, [7] 35 No 9 Wiesler, *Zeitsch anorg Chem* 1901 28 182 Walden, *Zeitsch physikal Chem* 1887 1, 529

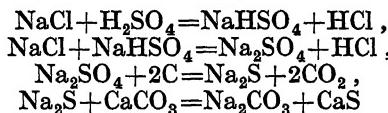
without, and an enlargement of the volume of air is unavoidable, in order to restore the equilibrium Again, in the open air suppose there were no aqueous atmosphere around the earth, only an azotic one = 23 inches of mercury, and an oxygenous one = 6 inches The air being thus perfectly dry, evaporation would commence with great speed The vapour first formed being constantly urged to ascend by that below, and as constantly resisted by the air, must, in the first instance, dilate the other two atmospheres, (for, the ascending steam adds its force to the upward elasticity of the two gases, and in part alleviates their pressure, the necessary consequence of which is dilatation) At last when all the vapour has ascended, that the temperature will admit of, the aqueous atmosphere attains an equilibrium, it no longer presses upon the other two, but upon the earth, the others return to their original density and pressure throughout In this case it is true, there would not be any augmentation of volume when aqueous vapour was combined with the air, humidity would increase the weight of the congregated atmospheres, but diminish their specific gravity under a given pressure One would have thought that this solution of the phenomenon upon my hypothesis was too obvious to escape the notice

vacuum, or in a current of hydrogen at 220° C., it evolves acetylene, leaving sodium carbide. The carbide is very reactive, readily undergoing decomposition with deposition of carbon, and decomposing water with evolution of acetylene.¹

Sodium carbonate, Na₂CO₃.—The carbonate is present in the ashes of sea-plants, its principal source prior to the French Revolution, when Le Blanc devised a method for its production. It is also found in the form of solid deposits,² and in solution in many natural waters. Pozzi-Escot³ believes the Peru deposits to have originated in the reduction to sodium sulphide, by means of plants and algae, of sodium sulphate dissolved from the soil, the sulphide formed being converted into sodium carbonate or sodium hydrogen carbonate by the action of carbon dioxide from the air, or from the decomposition of vegetable matter.

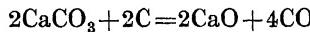
Sodium carbonate is manufactured from sodium chloride by three processes. Le Blanc's process, Solvay's ammonia-soda process, and the electrolytic process.⁴

Le Blanc's Process.—This process involves three stages—the conversion of sodium chloride into sodium sulphate, or "salt-cake process", the reduction of the sulphate to sulphide by means of carbon, and the conversion of the sulphide into sodium carbonate by the action of calcium carbonate, or "black-ash process", and the extraction of the sodium carbonate with water, or "lixiviation process".



The salt cake process takes place in two stages, the reaction represented by the second equation being carried on at a higher temperature in a reverberatory furnace. The hydrochloric acid constitutes a valuable by-product.

The sulphate prepared by the salt-cake process is pulverized, and mixed with an equal weight of chalk and half its weight of coal or coke. The mixture is then fused in a rotatory furnace. At first only carbon dioxide is evolved, but at the end of the operation carbon monoxide is generated, and burns as it escapes into the atmosphere.



The sodium carbonate is lixiviated with water to separate it from the calcium sulphide or "alkali waste," and from other impurities such as sodium chloride, sulphate, silicate, and aluminate, calcium oxide, sulphite, and thiosulphate, iron oxide, and alumina.

Ammonia-soda Process.—This process is said⁵ to have been devised by the apothecary Gerolamo Forni in 1836. It was perfected by Solvay, and on the continent of Europe it has largely displaced the older Le Blanc process. A solution of sodium chloride is treated alternately with ammonia and carbon dioxide under pressure, sodium

¹ Compare de Forcrand *ibid* 1895 120 1215 1897 124 1153 Matignon *ibid* 1897 125 1033

² Compare Reichert *Zeitsch Kryst Min* 1909 47 205

³ Pozzi Escot, *Bull Soc chim* 1919 [4] 25, 614

⁴ For full details of alkali manufacturing processes, see Lunge's *Manufacture of Sulphuric Acid and Alkali* 3rd ed (Guiney and Jackson 1911) vols II and III

⁵ Vanzetti *Chem Zeit* 1910 34, 229

no doubt true that the opposite powers of attraction and repulsion are frequently, perhaps constantly, energetic at the same instant, but the effect produced in those cases arises from the difference of the two powers. When the excess of the repulsive power above the attractive in different gases is comparatively small and insignificant, it constitutes that character which may be denominated neutral, and which I supposed to exist in the class of mixed gases which are not observed to manifest any sign of chemical union. I would not be understood to deny an energetic affinity between oxygen and hydrogen, &c in a mixed state, but that affinity is more than counterbalanced by the repulsion of the heat, except in circumstances which it is not necessary at present to consider.

Again, "Azotic gas comports itself with oxygen gas, in the changes occasioned by temperature and pressure, precisely like one and the same gas. Is it necessary to have recourse to a supposition which obliges us to admit so great a difference of action without an ostensible cause?" It is possible this may appear an objection to a person who does not understand the theory, but it never can be any to one who does. If a mixture of gas, such as atmospheric air, containing azote pressing

Sodium carbonate forms three hydrates. The *decahydrate* is monoclinic, and has the density 1.455,¹ other values being 1.446 at 17° C, and 1.493 at the temperature of liquid air.² At 20° C 100 grams of water dissolve 21.4 grams, reckoned as Na_2CO_3 . The *heptahydrate* appears to exist in both a rhombic and a metastable rhombohedral³ form, but only between narrow limits of temperature. Its solubility diminishes with rise of temperature. The solubility of the *monohydrate*⁴ at 50° C is 47.5 grams Na_2CO_3 in 100 grams of water. The transition-points of the hydrates are given by Wells and McAdam⁵ 10 to 7 (D), 32.0° C, 7 to 1 (F), 35.87° C, 10 to 1 (intersection CD and GF), 32.96° C. Some of their solubility-data are given in the table, and the solubility-curve in fig. 10 (p. 146).

$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$		$\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$		$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	
Temperature, °C	Grams Na_2CO_3 in 100 grams Water	Temperature, °C	Grams Na_2CO_3 in 100 grams Water	Temperature, °C	Grams Na_2CO_3 in 100 grams Water
27.84	34.20	30.85	43.50	29.86	50.53
29.33	37.40	31.82	45.16	31.80	50.31
30.35	40.12	32.86	46.28	35.37	49.67
31.45	43.25	34.87	48.22	37.91	49.11
31.72	44.21	35.15	49.23	40.93	48.52
32.06	45.61	35.62	50.08	43.94	47.98

The transition-temperature of the decahydrate to the heptahydrate is given by Richards and Fiske⁶ as 32.017° C.

According to Bezelius, and also Schindler,⁷ the decahydrate in air at 12.5° C becomes transformed into a *pentahydrate*. The existence of other hydrates described is even more doubtful. The boiling solution of sodium carbonate absorbs carbon dioxide from the atmosphere. Dubovitz⁸ found that exposure of the solid carbonate to atmospheric carbon dioxide and moisture for thirteen days produced between 15 and 20 per cent of the primary salt, Na_2HCO_3 , and that with a large excess of carbon dioxide and moisture complete conversion could be attained.⁹

Sodium hydrogen carbonate, NaHCO_3 . —The primary salt is an intermediate product in the ammonia-soda process, and can be prepared

¹ Complete Clarke Constants of Nature 2nd ed Washington 1888, p. 126. Schröder Dichtigkeitsmessungen Heidelberg 1873.

² Dewar Chem. News 1902 85 277.

³ Loewel Ann. Chim. Phys. 1851 [3] 33 382.

⁴ Fippe Dissertation, Heidelberg 1899.

Wells and McAdam J. Amer. Chem. Soc. 1907 29 721.

⁵ Richards and Fiske ibid. 1914 36 485.

⁶ Schindler Mag. Pharm. 33 14 319.

⁷ Dubovitz Chem. Zeit. 1921 45 890.

⁸ For a double carbonate of sodium and potassium see the section on potassium carbonate (p. 183).

waters on the surface of the globe were instantly expanded into steam , surely the action of gravity would collect the molecule into an atmosphere of similar constitution to the one we now possess , but suppose the whole mass of water evaporated amounted in weight to 30 inches of mercury , how could it support its own weight at the common temperature ? It would in a short time be condensed into water merely by its weight , leaving a small portion , such as the temperature could support , amounting perhaps to half an inch of mercury in weight , as a permanent atmosphere , which would effectually prevent any more vapour from rising , unless there were an increase of temperature Does not every one know that water and other liquids can exist in a Torricelian vacuum at low temperatures solely by the pressure of vapour arising from them ? What need then of the pressure of the atmosphere in order to prevent an excess of vapourisation ?

After having concluded that " without the pressure of the aerial atmosphere , liquids would pass to the elastic state , " Berthollet proceeds in the very next paragraph to shew that the quantity of vapour in the atmosphere may in fact be much *more* than would exist if the atmosphere were suppressed , and hence infers , " that the variations of the barometer oc-

A double salt with the normal carbonate, $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$,¹ occurs in Venezuela as *Urao*, and in Egypt as *Trona*. It is formed on concentrating a solution of the two salts in molecular proportions,² and has been observed³ to be a product of the efflorescence of the normal decahydrate during a period of twenty years.

Sodium percarbonate, $\text{Na}_2\text{C}_2\text{O}_6$ —The percarbonate is said⁴ to be formed by the electrolytic oxidation of the normal carbonate, but it has not been isolated by this method. A substance of the formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ is obtained by the interaction of 3 molecules of hydrogen peroxide in aqueous solution and 2 molecules of sodium carbonate, the product being subsequently dried *in vacuo*.⁵ Other percarbonates have been described,⁶ but their existence is still a subject of debate.

Sodium cyanide, NaCN —The cyanide is formed by the action of hydrocyanic acid on sodium hydroxide, by heating sodium ferrocyanide in absence of air, or with sodium carbonate and charcoal, from atmospheric nitrogen by heating anhydrous sodium carbonate with iron filings in air,⁷ by heating sodium in ammonia at 350°C , and converting the resulting sodamide into cyanide by heating with charcoal,⁸ and by the action of ammonia on a mixture of fused sodium cyanide, sodium, and charcoal, the sodium cyanamide, Na_2CN_2 , formed being converted by the charcoal into sodium cyanide.⁹

Sodium cyanide forms colourless crystals, very soluble in water, the weak acidic character of the hydrocyanic acid inducing hydrolytic dissociation, thus imparting to the solution a strong alkaline reaction, and an odour of hydrocyanic acid.¹⁰ The anhydrous salt is converted by boiling with 75 per cent alcohol into the dihydrate, a substance converted by slow evaporation over lime into the yellow, crystalline monohydrate.¹¹

For the heat of formation of sodium cyanide from its elements, Berthelot¹² gives 22.6 Cal, and Joannis¹³ 23.1 Cal. The heat of neutralization of hydrocyanic acid by sodium hydroxide is between 2.77 and 2.9 Cal, its low value being due to the heat absorbed by the ionization of the weak acid. At 9°C the heat of solution of the anhydrous salt is 0.5 Cal, and of the dihydrate 4.4 Cal.¹³ It is very poisonous.

Sodium thiocyanate, NaCNS —The thiocyanate can be prepared by the action of sodium carbonate on thiocyanic acid or ammonium thiocyanate, or by fusion of potassium ferrocyanide with anhydrous sodium thiosulphate.

The anhydrous salt forms very deliquescent, rhombic plates, its heat

¹ Chatard *Amer J Sci* 1889 [3] 38 59

² Compare Habermann and Kurtenacker *Zeitsch anorg Chem* 1909 63 65

³ Cumming *Chem News* 1910 102 311

⁴ Constan and Arthur von Hansen *Zeitsch Elektrochem* 1896 3, 137

⁵ Henkel & Co *British Patent* 1916 No 100997

⁶ Compare Tanatar *Ber* 1899 32 1544, Wolfenstein and Peltner, *Ber* 1908 41 280, Riesenfeld and Remhold *Ber* 1909 42 4377, Wolfenstein *Ber* 1910 43 639, Merck, *German Patent* 1909 No 213457

⁷ Tauber *Ber* 1899 32 3150

⁸ Behringer *German Patent* No 90999

⁹ Rössler *German Patents* Nos 124977 and 126241

¹⁰ Compare James Walker *Zeitsch physikal Chem* 1900 32 137

¹¹ Joannis *Ann Chim Phys* 1882 [5] 26, 484

¹² Berthelot *Compt rend*, 1880 91 79

¹³ Joannis *loc cit*

does not sensibly condense the volume of any mixture, nor give out heat, nor change the properties of the ingredients, its effect may be called *solution* or *dissolution*, for instance, when oxygen gas and azotic gas are mixed in due proportion, they constitute atmospheric air, in which they retain their distinguishing properties

It is upon this supposed *solution* of one elastic fluid in another that I intend to make a few observations That I have not misrepresented the author's ideas, will, I think, appear from the following quotations "When different gases are mixed, whose action is confined to this solution, no change is observed in the temperature, or in the volume resulting from the mixture, hence it may be concluded, that this mutual action of two gases does not produce any condensation, and that it cannot surmount the effort of the elasticity, or the affinity for caloric, so that the properties of each gas are not sensibly changed— " " Although both the solution and combination of two gases are the effect of a chemical action, which only differs in its intensity, a real difference may be established between them, because there is a very material difference between the results the combination of two gases always leads to a condensation of their volume, and

Sodium hypoborate, NaH_2BO —On cooling the mixture produced by the interaction of a very concentrated solution of potassium hydroxide and boron hydride, B_4H_{10} , the very deliquescent sodium hypoborate is obtained¹

Sodium borates—The anhydrous *metaborate*, NaBO_2 , is formed by fusing borax with sodium carbonate, being obtained in hexagonal prisms, m p² 966°C , density³ 0.2571 between 17° and 97°C . When the syrup-like solution obtained by concentrating equivalent proportions of sodium hydroxide and boric acid or borax is allowed to crystallize over concentrated sulphuric acid, the *tetrahydrate* separates in triclinic crystals. The *dihydrate*⁴ and other hydrates⁵ have also been described. The aqueous solution of the metaborate has an alkaline reaction, due to hydrolytic dissociation⁶. The *orthoborate* is formed by fusing boric anhydride with sodium peroxide⁷.

The most important borate of sodium is *disodium tetraborate* or *borax*, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, found in Thibet as the mineral *tincal*, and also in California. The native variety is purified by crystallization, but most of the borax of commerce is obtained by fusing native boric acid with sodium carbonate.

The anhydrous salt is obtained by heating the decahydrate, and is a white substance of density⁸ 2.367. Its melting-point is given as 561°C ,⁹ 730°C ,¹⁰ 741°C ,¹¹ and 878°C ,¹² the fused substance solidifying to a colourless, transparent, vitreous mass known as the "borax bead". In the melted state it dissolves metallic oxides, producing characteristic colorations, and finds application in analysis. It is also employed in soldering metals to remove the superficial layer of oxide, and to prevent oxidation during the process by excluding the air. Its specific heat is 0.229 between 17° and 47°C (Kopp¹³), and 0.2382 between 16° and 98°C (Regnault¹⁴). Its heat of formation is 748.1 Cal.¹⁵

The *decahydrate* or ordinary borax forms monoclinic crystals of density 1.723 (Hassenfratz¹⁶), 0.1694 at 17°C , and 1.728 at the temperature of liquid air (Dewar¹⁷). Its specific heat¹⁸ is 0.385 between 19° and 50°C . A *pentahydrate* belonging to the rhombohedral division of the hexagonal system crystallizes above 60°C . Its density¹⁹ is 1.815. The pentahydrate is stable from 60°C , the transition-point from the decahydrate, to 125°C . At 130°C the stable form is the *trihydrate*,

¹ Stoel and Kuss *Ber* 1914 47 810, see potassium hypoborate p 180

² van Klooster *Zeitsch anorg Chem* 1916 69 122

³ Regnault *Pogg Annalen* 1841 53 60 243

⁴ Dukelski *Zeitsch anorg Chem* 1906 50 38

Atterberg *ibid*, 1906 48 367

⁶ Compare James Waller *Zeitsch physikal Chem* 1900 32 137

⁷ Mixter *Amer J Sci* 1908 [4] 26 125

⁸ Filhol, *Ann Chim Phys* 1847 [3] 21 415

⁹ Carnelley *Trans Chem Soc* 1878 33 273

¹⁰ Ponomaryv *Zeitsch anorg Chem* 1914 89 383

¹¹ Dana and Foote *Trans Faraday Soc* 1920 15 186

¹² Victor Meyer and Riddle *Bei* 1893 26 2448

¹³ Kopp *Annalen Suppl* 1864-65 3 1 280

¹⁴ Regnault *Pogg Annalen* 1841 53 60, 243

¹⁵ Berthelot *Ann Chim Phys* 1873 [4] 29 470

¹⁶ Compare Clarke *Constants of Nature*, 2nd ed Washington 1888 1, 107

¹⁷ Dewar *Chem News* 1902 85 277

¹⁸ Kopp *loc cit*

¹⁹ Payen, *Jahresber*, 1828, 171

elastic fluids *are* endued with the force of cohesion; but this he applies only to heterogeneous particles. He certainly does not mean that the particles of homogeneous elastic fluids possess the force of cohesion.

Newton has demonstrated from the phenomena of condensation and rarefaction that elastic fluids are constituted of particles, which repel one another by forces which increase in proportion as the distance of their centres diminishes. In other words, the forces are reciprocally as the distances. This deduction will stand as long as the Laws of elastic fluids continue to be what they are. What a pity it is that all who attempt to reason, or to theorise respecting the constitution of elastic fluids, should not make themselves thoroughly acquainted with this immutable Law, and constantly hold it in their view whenever they start any new project! When we contemplate a mixture of oxygenous and hydrogenous gas, what does Berthollet conceive, are the particles that repel each other according to the Newtonian Law? The mixture *must* consist of such, and he ought in the very first instance to have informed us what constitutes the unity of a particle in his solution. If he grants that each particle of oxygen retains its unity, and each particle of hydrogen does the

water it yields hydrogen peroxide. At 22° C its solubility is 71 grams of $\text{Na}_2\text{B}_4\text{O}_8$ in 100 grams of water, the solution being strongly alkaline.

DETECTION AND ESTIMATION OF SODIUM.

All sodium salts impart a characteristic yellow coloration to the Bunsen flame, the test being so delicate as to detect 3×10^{-10} grams. The extreme delicacy of the test and the wide distribution of traces of sodium chloride throughout the atmosphere render the persistence or otherwise of the coloration an important factor in determining the presence or absence of sodium in the substance under examination. In the spectroscope, sodium gives a yellow line, coincident with the D-line of the solar spectrum.

Most salts of sodium are soluble in water, but the pyroantimonate, $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$, dissolves only to the extent of 1 part in 350 parts of boiling water. It is produced by addition of potassium pyroantimonate to a neutral or alkaline solution of a sodium salt. The double chloride with tin, and the double sulphite with platinum, $\text{Na}_6\text{Pt}(\text{SO}_3)_4 \cdot 7\text{H}_2\text{O}$, are less soluble than the corresponding potassium salts.

In quantitative analysis sodium is estimated as sulphate, formed by evaporation with concentrated sulphuric acid. If potassium be present, its amount is determined by precipitation as double chloride with platinum from the solution of the mixed sulphates.¹

The salts of sodium react with a solution of potassium nitrite and the nitrates of bismuth and caesium, yielding a yellow, crystalline precipitate of the formula $5\text{Bi}(\text{NO}_2)_3 \cdot 9\text{CsNO}_2 \cdot 6\text{NaNO}_2$. This reaction is applicable to the detection and estimation of sodium.²

¹ On the separation from potassium and rubidium, compare Wernadski, *Bull Soc franç Min* 1913 36 258

² Ball, *Trans Chem Soc*, 1909 95, 2126, 1910 97, 1408

cognisable to any of the senses. It certainly requires an extraordinary stretch of the imagination to admit the affirmative.

One great reason for the adoption of this or any other theory on the subject, arises from the phenomena of the evaporation of water. How is water taken up and retained in the atmosphere? It cannot be in the state of vapour, it is said, because the pressure is too great there must therefore be a true chemical solution. But when we consider that the surface of water is subject to a pressure equal to 30 inches of mercury, and besides this pressure there is a *sensible* affinity between the particles of water themselves, how does the *insensit* affinity of the atmosphere for water overcome both these powers? It is to me quite inexplicable upon this hypothesis, the leading object which is to account for this very phenomenon. Further, if a particle of air has attached a particle of water to it, what reason can I assign why a superior particle of air should rob an inferior one of its property, when each particle possesses the same power? If a portion of common salt be dissolved in water and a little muriatic acid added, is there any reason to suppose the additional acid displaces that already combined with the soda, and that upon evaporation the salt is not obtained with

at dull redness, and subsequently raising the temperature of small portions of the carbonaceous mass to bright redness, the molten metal being tapped off. The fused hydroxide can also be allowed to flow over heated charcoal, and the metal distilled off.¹

When equivalent weights of sodium and potassium hydroxide are mixed, and fused in absence of air, sodium monoxide is formed, hydrogen evolved, and potassium distils at a temperature of about 670° C. The metal can be condensed, and the process is claimed to be applicable to its manufacture.²

Latterly the production of potassium by the electrolytic process has become of industrial importance, partly on account of the purity of the product, and partly because the attendant risk is much less than with the chemical methods. The ordinary Castner³ process for the isolation of sodium is inapplicable to potassium, Lorenz⁴ having shown that part of the potassium is dissolved in the molten state by the fused hydroxide, and part is vaporized and after condensation in minute drops is diffused throughout the liquid mass. The effect is that the liberated metal tends to combine with the anion at the anode. The difficulty is avoided by surrounding the iron-wire cathode with a cylinder of magnesite to prevent diffusion of the metal to the anode, by employing as low a temperature as possible, and by excluding air. An anode of sheet iron is immersed in the fused hydroxide outside the magnesite chamber. As substitutes for the hydroxide, potassium nitrate,⁵ and also potassium chloride with an admixture of fluoride to lower the melting point,⁶ are employed. With the nitrate the cathode is an aluminium vessel.

Physical Properties — Potassium is a soft, silver white⁷ metal of high lustre. Its melting point is given as 60° C.,⁸ 62 4° C.,⁹ 62 5° C.,¹⁰ and 63 5° C.¹¹ A wide discrepancy exists between the values given for the boiling-point, among them being 667° C.¹², 667° C. at 760 mm pressure,¹³ 719° to 731° C.,¹⁴ 757 5° C.,¹⁵ 365° C. at 0 mm.,¹⁶ and about 90° C. in the vacuum of the cathode light.¹⁷ For the density are recorded the values 0 8629¹⁸ and 0 859¹⁹ at 0° C., 0 8621²⁰ at 20° C., and 0 851

¹ Netto *British Patents* 1887 Nos 14602 and 17412

Wickel and Loebel *German Patent* 1919 No 307175

³ Castner *British Patent*, 1890 No 13356

⁴ Lorenz and Clarke *Zeitsch Elektrochem* 1903 9 269 compare Le Blanc and Biode *ibid* 1902 8 817

Darling and Follett *German Patent* No 83097

⁶ Stoerck *ibid* No 68335

⁷ Bornemann (*Zeitsch angew Chem* 1922 35 227) has described a method of preparing and preserving the metal un tarnished

⁸ Masing and Lummann *Zeitsch anorg Chem* 1910 67 183

⁹ Guilletti and Pitani *Zeitsch Metallur* 1919 II 1

¹⁰ Bunsen *Annalen* 1863 125 368 Holt and Sims *Trans Chem Soc* 1894 65 432 Kurnikoff and Pushin *Zeitsch anorg Chem* 1902 30 109 van Blieswyk *ibid*, 1912 74 152

¹¹ Rengade *Compt rend* 1913 156 1897 *Bull Soc chim* 1914 [4] 15 130

¹² Permin *Trans Chem Soc* 1889 55 326

¹³ Hansen *Ber* 1909 42 210

¹⁴ Arnall and Williams *Trans Chem Soc* 1879 35 563 1880 37 125

¹⁵ Ruff and Johannsen *Ber* 1905 38 3601

¹⁶ Hansen *loc cit*

¹⁷ Kraft and Beigfeld *Ber* 1905, 38 254

¹⁸ Vicentini and Omodci *Wied Annalen Berbl* 1888 12 176

¹⁹ Hackspill *Compt rend* 1911 152, 259

²⁰ Richards and Brink *J Amer Chem Soc*, 1907 29, 117

tached to it, but this is impossible, one half of the atoms of oxygen must then take two of hydrogen, and the other half, one each. But the former would be specifically lighter than the latter, and ought to be found at the top of the solution; nothing like this is however observed on any occasion.

Much more might be advanced to shew the absurdity of this doctrine of the solution of one gas in another, and the insufficiency of it to explain any of the phenomena; indeed I should not have dwelt so long upon it, had I not apprehended that respectable authority was likely to give it credit, more than any arguments in its behalf derived from physical principles.

Dr Thomson, in the 3d Edition of his System of Chemistry, has entered into a discussion on the subject of mixed gases, he seems to comprehend the excellence and defects of my notions on these subjects, with great acuteness. He does not conclude with Berthollet, that on my hypothesis, "there would not be any augmentation of volume when aqueous and ethereal vapour was combined with the air," which has been so common an objection. There is however one objection which this gentleman urges, that shews he does not completely understand the

surface of the metal soon tarnishes, owing to the effect of moisture. The metal also combines energetically with oxygen and the halogens, an example being the liberation of silicon and boron from their oxides and chlorides. Its solution in liquid ammonia reacts with ozone.¹

Potassium Ion—With the exception of rubidium and caesium, potassium has the greatest electroaffinity or tendency to ionization, a fact regarded by Abegg and Bodländer as according with the ready solubility of most of its salts, and the comparatively slight tendency of its ions to form complex salts or hydrates. The potassium salts are strong electrolytes, being highly dissociated in dilute aqueous solution. Only those with coloured anions yield coloured solutions, an indication that the potassium ion is colourless. The conductivity of the potassium ion is 64.5 at 18° C., and 74.8 at 25° C. The transport-number² is 0.514.

Atomic Weight—In connexion with the atomic weight of sodium, reference has been made to the general methods employed by Berzelius, by Stas, and by Marignac in determining the atomic weights of sodium, potassium, silver, chlorine, bromine, and iodine. At this point it will suffice to summarize the results obtained by these methods, and those derived from the work of modern investigators.

There are numerous early determinations of the composition of potassium chlorate, giving the ratio $\text{KClO}_3 : \text{KCl} = 100 : x$, where $x =$

Experimenter	Year	$\text{KClO}_3 : \text{KCl} = 100 : x$, where $x =$
Berzelius ³	1818	60.851 ± 0.0006
Penny ⁴	1839	60.8225 ± 0.0014
Pelouze ⁵	1842	60.843 ± 0.0058
Marignac ⁶	1842	60.839 ± 0.0018
Gerhardt ⁷	1845	60.8757 ± 0.0020
"	"	60.9487 ± 0.0011
Maumene ⁸	1846	60.791 ± 0.0009
Stas ⁹	1860	60.8428 ± 0.0012
"	"	60.8490 ± 0.0017

In Stas's first series of experiments the chlorate was decomposed by heat, in the second, it was decomposed by hydrochloric acid. From the foregoing results Clarke¹⁰ has computed the weighted mean (p. 8)

$$\text{KClO}_3 : \text{KCl} = 100 : 60.846 \pm 0.00038$$

¹ Compare sodium p. 86.

² Tolman *J. Amer. Chem. Soc.* 1911, 33, 121.

³ Berzelius *Trommsdorff's N. J. Pharm.* 1818, II, 2, 44. *Pogg. Annalen* 1826, 8, 1. *Lehrbuch der Chemie* 5th ed. Dresden 1843-1848, 3, 1189.

⁴ Penny *Phil. Trans.* 1839, 129, 20.

⁵ Pelouze *Compt. rend.* 1842, 5, 959.

⁶ Marignac *Oeuvres Complètes* Geneva 1902, I, 57.

⁷ Gerhardt *Compt. rend.* 1845, 21, 1280.

⁸ Maumene *Ann. Chim. Phys.* 1846, [3], 18, 71.

⁹ Stas, *Oeuvres Complètes*, Brussels, 1894, I, 404.

¹⁰ Clarke *A Recalculations of the Atomic Weights* Washington Smithsonian Miscellaneous Collections, 2nd ed., 1897; 3rd ed., 1910.

root of the spaces inversely, that is, as $\sqrt{2}$ 1, or as 1 26 I nearly. In such a mixture as has just been mentioned, then, the common hypothesis supposes the pressure of each particle of gas to be 1 26, whereas mine supposes it only to be 1, but the sum of the pressure of both gases on the containing vessel, or any other surface, is exactly the same on both hypotheses

Excepting the above objection, all the rest which Dr Thomson has made, are of a nature not so easily to be obviated,—he takes notice of the considerable time which elapses before two gases are completely diffused through each other, as Berthollet has done, and conceives this fact, makes against the supposition, that one gas is as a vacuum to another He further objects, that if the particles of different gases are inelastic to each other, then a particle of oxygen coming into actual contact with one of hydrogen, ought to unite with it, and form a particle of water, but, on the other hand, he properly observes, that the great facility with which such combinations are effected in such instances as a mixture of nitrous and oxygen gas, is an argument in favour of the hypothesis—Dr Thomson finds another objection upon the facility of certain combinations, when one of the ingredients is in a *nascent* form,

Experimenter	Year	Ag KBr=100 x , where $x =$
Marignac ¹	1843	110 343 0 005
Stas ²	1865	110 346 \pm 0 002

The weighted mean is

$$\text{Ag KBr}=100 \quad 110\ 3459 \pm 0\ 0019 \quad (\text{F})$$

Five analyses of potassium iodide by Marignac ³ in 1843 gave

$$\text{Ag KI}=100 \quad 158\ 800 \quad (\text{G})$$

From the foregoing seven mean results lettered from A to G the atomic weight of potassium can be induced. For this purpose the antecedent data calculated by Stas from his experiments have been chosen, (O=16), Cl=35 457, Br=79 952, I=126 850, Ag=107 930. The values obtained for the atomic weight of potassium are

$$\begin{array}{llll} (\text{A}) \ 39\ 136 & (\text{C}) \ 38\ 739 & (\text{E}) \ 39\ 113 & (\text{G}) \ 39\ 038 \\ (\text{B}) \ 39\ 438 & (\text{D}) \ 39\ 138 & (\text{F}) \ 39\ 144 & \end{array}$$

The values (B) and (C), derived from analyses of potassium bromate and iodate, are obviously worthless. The results (A), (D), and (F) depend mainly on the careful work of Stas, and their arithmetic mean is 39 139. The results (E) and (G) are based on Marignac's work on potassium chloride and iodide, and approximate reasonably to those of Stas. Excluding (B) and (C), the arithmetic mean of the results is

$$\text{K}=39\ 113$$

From his own experiments Stas induced the value K=39 142, and recalculation in terms of O=16 of the value accepted as the atomic weight of potassium for many years gives 39 14 or 39 15.

The work of modern investigators, particularly that of Richards and his coadjutors at Harvard, has proved Stas's value for the atomic weight of silver to be too high, and his relative values for silver and chlorine to be erroneous. These inaccuracies vitiate the preceding calculations, but there would be no advantage in deriving them from more accurate antecedent data, as modern research has disclosed appreciable errors in even the most painstaking of the earlier work, and furnished more reliable ratios for inducing the atomic weight of potassium. In the subjoined account the calculations have been made with the atomic weights O=16 000, Ag=107 880, Cl=35 457, Br=79 916, N=14 008.

In connection with their work on cesium, Richards and Archibald ⁴ in 1903 made two analyses of potassium chloride, the results being

$$\text{AgCl KCl}=100 \quad 52\ 0215,$$

¹ Marignac *Oeuvres Complètes* Geneva 1902 i 82

² Stas *Oeuvres Complètes* Brussels 1894 i 747

³ Marignac *Oeuvres Complètes* Geneva 1902 i 86

⁴ Richards and Archibald *Proc Amer Acad* 1903 38 47

air, but the same ball, being made into a thousand smaller ones of $\frac{1}{10}$ of an inch diameter, and falling with the same velocity, meets with 10 times the resistance it did before because the force of gravity increases as the *cube* of the diameter of any particle, and the resistance only as the *square* of the diameter. Hence it appears, that in order to increase the resistance of particles moving in any medium, it is only necessary to divide them, and that the resistance will be a maximum when the division is a maximum. We have only then to consider particles of lead falling through air by their own gravity, and we may have an idea of the resistance of one gas entering another, *only the particles of lead must be conceived to be infinitely small*, if I may be allowed the expression. Here we shall find great resistance, and yet no one, I should suppose, will say, that the air and the lead are mutually elastic.

The other two objections of Dr Thomson, I shall wave the consideration of at present.

Mr Murray has lately edited a system of chemistry, in which he has given a very clear description of the phenomena of the atmosphere, and of other similar mixtures of elastic fluids. He has ably discussed the different theories that have been proposed on the subject,

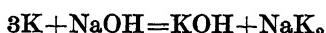
Neglecting the work of Richards and Archibald, which lacks the experimental accuracy of the later investigations, five modern values for the atomic weight of potassium fall within the limits of 39.095 and 39.098, and indicate the great probability of the value

K=39.096

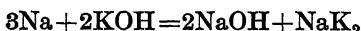
The current table of the International Committee on Atomic Weights gives¹

K=39.10

Alloys of Potassium and Sodium²—Potassium and sodium unite to an alloy of the formula Na_2K ³. In absence of air at 200° to 250° C, potassium reacts with sodium hydroxide to form a liquid alloy NaK_2 .⁴



At 350° C sodium and potassium hydroxide interact in accordance with the equation



At 225° to 275° C the reaction is different, and is expressed by the equation



On exposure to air these alloys ignite instantly

COMPOUNDS OF POTASSIUM

Potassium hydride, KH—Moissan⁵ prepared the hydride by a method analogous to that employed by him for the corresponding sodium derivative, the excess of potassium being dissolved by liquid ammonia. Ephraim and Michel⁶ passed hydrogen into potassium at 350° C, and found the reaction to be promoted by the presence of calcium. The hydride forms white crystals of density 0.80. The vapour-tension for each temperature-interval of 10° between 350° and 410° C corresponds with the values 56, 83, 120, 168, 228, 308, and 430 mm respectively.⁷ In chemical properties potassium hydride resembles the sodium compound, but is less stable. Its stability is greater than that of rubidium hydride or caesium hydride. Carbon dioxide converts it into potassium formate.

Potassium fluoride, KF—The fluoride is produced by the interaction of hydrofluoric acid and potassium carbonate or hydroxide by heating potassium silicofluoride or borofluoride with lime, and by the action of potassium on fluorine, hydrofluoric acid, or silicon fluoride or boride.

The anhydrous salt forms crystals belonging to the cubic system,

¹ Compare Hinrichs, *Compt. rend.* 1909 148 484 Dubreuil *Bull. Soc. chim.* 1910 [4] 7 119, W A Noyes and H C P Weber *J. Amer. Chem. Soc.* 1908 30 13 for potassium amalgam see this series Vol III

² Van Bleiswyk *Zeitsch. anorg. Chem.* 1912 74 152

³ Jaubert *Ber.* 1908 41 4116

⁴ Moissan *Compt. rend.* 1902 134 18 compare Troost and Hautefeuille *ibid.* 1874 78 807 Elster and Geitel *Physikal. Zeitsch.* 1910 11 257

⁵ Ephraim and Michel *Helv. Chim. Acta* 1921 4 762

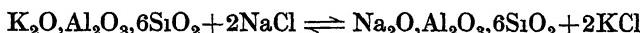
⁶ Compare Keyes, *J. Amer. Chem. Soc.*, 1912 34, 779

retained in mixture by that force of adhesion, which, exerted at the surfaces of many bodies, retains them in contact with considerable force." He supports these notions at length by various observations, and repeats some of the observations of Berthollet, whose doctrine on this subject, as has been seen, is nearly the same.

Before we animadadvert on these principles, it may be convenient to extend the first a little farther, and to adopt as a maxim, "that between the particles of *pure* gases, which are capable under any circumstances of combining, an attraction must always be exerted." This, Mr Murray cannot certainly object to, in the case of steam, a pure elastic fluid, the particles of which are known in certain circumstances to combine. Nor will it be said that steam and a permanent gas are different, for he justly observes, "this distinction (between gases and vapours) is merely relative, and arises from the difference of temperature at which they are formed, the state with regard to each, while they exist in it, is precisely the same." Is steam then constituted of particles in which the attraction is so far exerted as to prevent their separation? No they exhibit no traces of attraction, more than the like number of particles of oxygen do, when in

("Abraumsalze") contain 55 to 65 per cent of carnallite, associated with 20 to 25 per cent of rock-salt, 10 to 20 per cent. of kieserite, $MgSO_4 \cdot H_2O$, and 2 to 4 per cent. of tachydrite, $CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$. The technical preparation of potassium chloride from these deposits depends on the ready solubility of carnallite, and the crystallization of potassium chloride from hot saturated solutions of this substance.¹ Kainite is employed as a source of potassium chloride, and the compound is also obtained by fractional crystallization of the salts present in sea-water and in the ash of seaweed.

A process for the production of potassium chloride from orthoclase was patented by Bassett,² but has not been worked technically. It was discovered independently and investigated by Ashcroft,³ and consists in heating finely divided orthoclase with sodium chloride in equal proportion by weight at 900° to 1000° C., 85 per cent of the potassium in the mineral being replaced by sodium in accordance with the scheme



The potassium chloride can be separated from the insoluble sodium felspar by lixiviation, and from the excess of sodium chloride by fractional crystallization. This process might afford a new method for the manufacture of potassium chloride. It has also been found possible to extract the salt from the dust of the blast-furnace.⁴

Potassium chloride forms colourless cubes, and has also been obtained in octahedra, rhombododecahedra, and icositetrahedra. Its melting-point is given as 762° C.,⁵ 772.8° C.,⁶ 774° C.,⁷ 775° C.,⁸ 778° C.,⁹ and 790° C.¹⁰ It volatilizes without decomposition, the molecular weight derived from the vapour density,¹¹ and also that from the depression of the freezing point of mercuric chloride,¹² corresponding with the simple formula KCl . For the density are given the mean value 1.977,¹³ and also 1.989 at 16° C.,¹⁴ 1.991 at 20° C.,¹⁵ 1.994 at 20.4° C.,¹⁶ 1.951 at 23.4° C.,¹⁷ 1.612 at the melting point.¹⁸ The specific heat is given as 0.171 between 13° and 46° C.,¹⁹ 0.1730 between 14° and 99° C.,²⁰ 0.1840 between 20° and 726° C., and for the fused salt 0.2671 between 80° and

¹ Compare van't Hoff and Meyerhoffer *Sitzungsber K Akad Wiss Berlin* 1897 487 *Zeitsch physikal Chem*, 1899 30 64 Meyerhoffer, German Patents 1896 Nos 92812 and 98344

² H P Bassett *U S A Patent* 1913, No 1072686

³ Ashcroft *Chem Trade J* 1917 61 529

⁴ Chance, *ibid* 1918 62, 44 *J Soc Chem Ind* 1918, 37, 87
Ramsay and Eumorfopoulos *Phil Mag* 1896 41 360

⁵ Plato *Zeitsch physikal Chem* 1906 55 721

⁶ Schruber *Jahrb Min Berl Bd* 1919 43 132

⁷ Arndt *Zeitsch Elektrochem* 1906 12 337 Haigh *J Amer Chem Soc* 1912 34

⁸ 1137 Korring *Jahrb Min Berl Bd* 1914 37 51

⁹ Huttner and Tammann *Zeitsch anorg Chem* 1905 43 215

¹⁰ Schemtschuschny and Rambach *J Russ Phys Chem Soc* 1909 41 1785

¹¹ Nernst *Nachr K Ges Wiss Gottingen* 1903 75

¹² Beckmann *Zeitsch anorg Chem* 1907 55 180

¹³ Compare Clarke *Constants of Nature* 2nd ed Washington 1888 1 20 and 21

¹⁴ Retgers *Zeitsch physikal Chem* 1889 3 289

¹⁵ Haigh *J Amer Chem Soc*, 1912 34 1137

¹⁶ Krickmeyer *Zeitsch physikal Chem* 1896 21, 53

¹⁷ Buchanan *Proc Chem Soc* 1905 21 122

¹⁸ Quincke *Pogg Annalen* 1869 138 141

¹⁹ Kopp, *Annalen Suppl* 1864-5, 3, 1 289

²⁰ Regnault *Pogg Annalen* 1841, 53 60 243

facility, nay, these last exercise this solvent power with more effect than the former, for, hydrogen can draw up carbonic acid from the bottom to the top of any vessel, notwithstanding the latter is 20 times the specific gravity of the former. One would have thought that a force of adhesion was more to be expected in the particles of steam, than in a mixture of hydrogen and carbonic acid. But it is the business of those who adopt the theory of the mutual solution of gases to explain these difficulties.

In a mixture where are 8 particles of oxygen for 1 of hydrogen, it is demonstrable that the central distances of the particles of hydrogen are at a medium twice as great as those of oxygen. Now supposing the central distance of two adjacent particles of hydrogen to be denoted by 12, query, what is supposed to be the central distance of any one particle of hydrogen from that one particle, or those particles of oxygen with which it is connected by this weak chemical union? It would be well if those who understand and maintain the doctrine of chemical solution would represent how they conceive this to be, it would enable those who are desirous to learn, to obtain a clear idea of the system, and those who are dissatisfied with it, to point out its defects with

The mean density is 2 690,¹ other values found being 2 756 at 20° C,² 2 679 at 23 4° C,³ and 2 73 at 25° C.⁴ The specific heat is 0 1132 between 16° and 98° C,⁵ or 0 102 between the temperature of liquid air and 15° C.⁶ The molecular electric conductivity of potassium bromide between 745 2° and 868 6° C is given by the formula⁷

$$\mu_t = 90\ 09 + 0\ 1906(t - 750)$$

The heat of formation of potassium bromide from the elements is given as 95 3 Cal⁸ and 95 6 Cal⁹. At 20° C 100 grams of water dissolve 65 grams of the bromide¹⁰, and at 25° C 100 grams of ethyl alcohol dissolve 0 142 gram.¹¹

In aqueous solution potassium bromide reacts with bromine, *polybromides* with the formulæ KBr₃ and KBr₅ being formed in solution.¹² In the neighbourhood of its melting-point the salt evolves bromine freely.¹³ Potassium bromide finds application in medicine as a soporific, and in photographic development as a "restrainer".

Potassium iodide, KI —The iodide is obtained by neutralizing the carbonate with hydroiodic acid, and also by the interaction of potassium hydroxide and iodine, the iodate simultaneously produced being converted into iodide by heat or by the action of a reducer such as carbon.



It is manufactured by the action of iron filings on iodine in presence of water, the soluble iodide Fe₃I₈ formed being decomposed by potassium hydroxide, a process accompanied by precipitation of the oxide Fe₃O₄ and formation of a solution of potassium iodide. The salt crystallizes on concentration of the aqueous solution. It can also be prepared from the ashes of seaweed, and from the iodate present in Chile saltpetre.

Potassium iodide forms crystals belonging to the cubic system, melting at 677 3° C,¹⁴ 680° C,¹⁵ 684 1° C,¹⁶ 705° C,¹⁷ or 722 7° C.¹⁸ Its density is given by various investigators as 3 079,¹⁹ 3 048 at 24 3° C,²⁰ and 3 115 at 25° C.²¹ The specific heat is given as 0 0766,²² and 0 0819

¹ Schroder *Dichtigkeitsmessungen* Heidelberg 1873 compare Clarke *Constants of Nature* 2nd ed Washington 1888 i 31

- Krickmeyer *Zeitsch physikal Chem.*, 1896 21 53

³ Buchanan *Proc Chem Soc* 1905 21 122

⁴ Richards and Mueller *J Amer Chem Soc* 1907 29 639 compare Brunner *ibid* 1904 38 350 Lorenz, Frei and Jabs *Zeitsch physikal Chem* 1908 61 468

⁵ Regnault *Pogg Annalen* 1841 53 60 243

⁶ Nordmeyer *Ber Deut physikal Ges* 1908 6 2021

⁷ Jaeger and Kapma *Zeitsch anorg Chem* 1920 113, 27

⁸ Thomsen *J prakt Chem* 1875 [2] ii 242

⁹ Berthelot *Thermochimie Paris* 1897 i 181

¹⁰ de Coppel *Ann Chim Phys* 1883 [5] 30 416

¹¹ Turner and Bissell *Trans Chem Soc* 1913 103 1904

¹² Bonicke *Zeitsch Elektrochem* 1905 ii 57

¹³ Guareschi *Atti R Accad Sci Torino* 1913 48 735

¹⁴ McCrae *Wied Annalen* 1895 55 95

¹⁵ Huttner and Fammann *Zeitsch anorg Chem* 1905 43 215

¹⁶ Rassow, *Zeitsch anorg Chem* 1920 114 117

¹⁷ Ruff and Plato *Ber* 1903 36 2357

¹⁸ McCrae *loc cit*

¹⁹ Compare Clarke *Constants of Nature* 2nd ed Washington 1888 i 34

²⁰ Buchanan *Proc Chem Soc* 1905 21 122

²¹ Baxter and Brink *J Amer Chem Soc* 1908 30 46

²² Nernst and Lindemann, *Sitzungsber K Akad Wiss Berlin* 1910 247

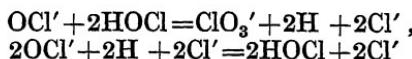
the position which I maintain, that if the atmosphere were annihilated, we should have little more aqueous vapour than at present exists in it Upon which I shall only remark, that if either of those gentlemen will calculate, or give a rough estimate upon their hypothesis, of the quantity of aqueous vapour that would be collected around the earth, on the said supposition, I will engage to discuss the subject with them more at large

In 1802, Dr Henry announced a very curious and important discovery, which was afterwards published in the Philosophical Transactions, namely, *that the quantity of any gas absorbed by water is increased in direct proportion to the pressure of the gas on the surface of the water* Previously to this, I was engaged in an investigation of the quantity of carbonic acid in the atmosphere, it was matter of surprise to me that lime water should so readily manifest the presence of carbonic acid in the air, whilst pure water by exposure for any length of time, gave not the least traces of that acid I thought that length of time ought to compensate for weakness of affinity In pursuing the subject I found that the quantity of this acid taken up by water was greater or less in proportion to its greater or less density in the gaseous mixture, incumbent

chlorite is formed analogously to that of sodium hypochlorite by the action of chlorine on a dilute aqueous solution of the hydroxide at low temperatures, by the interaction of potassium salts and bleaching-powder solution, and by the electrolysis of potassium-chloride solution without a diaphragm. It is also formed to some extent by passing an alternating current through a solution of potassium chloride¹. The heat of formation of the substance in aqueous solution is given as 84.35 Cal² and 88.0 Cal³. This solution was formerly employed as a bleaching agent, under the name "Eau de Javelle".

Potassium chlorate, $KClO_3$ —The chlorate is obtained by methods similar to those employed for the corresponding sodium salt. The electrolysis of the chloride⁴ affords a means of manufacture, and it is also obtained by the interaction of potassium chloride and calcium chlorate. Large quantities are made by the electrolytic oxidation of sodium chloride to chlorate, and conversion of this salt into potassium chlorate by treatment with potassium chloride. Sodium chlorate is much more soluble than potassium chlorate, so that the electrolytic process is not impeded by crystallization of the salt.

The electrochemical formation of chlorate from hypochlorite is regarded by Knibbs and Palfreeman⁵ as involving two reactions, represented by the equations



The net result is the disappearance of three hypochlorite ions, with formation of 1 chlorate ion and 2 chloride ions. Although apparently termolecular, the first reaction is unimolecular, since the concentration of the hypochlorous acid remains constant. The second reaction is practically instantaneous⁶. Chloride can be produced by the electrolysis of chlorate, possibly in accordance with the equation



M representing an atom of a univalent metal. The formation of chloride is promoted by rise of temperature, but is almost inhibited by the presence of chromate⁷.

Potassium chlorite forms monoclinic crystals,⁸ its melting point being given as 357.10° C,⁹ 370° C,¹⁰ and 372° C.¹¹ When a solution obtained by treatment of crude Californian petroleum with concentrated sulphuric acid and dilution with water is added to a solution in water of the ordinary tabular potassium chlorate, and the mixture con-

¹ Coppadore *Gazzetta* 1905, 35 n. 604

² Berthelot *Ann Chim Phys.* 1875 [5] 5, 337

³ Ihssen *Thermochemistry* (Longmans 1908) 328

⁴ Wallach *Zeitsch Elektrochem.* 1906, 12, 677. See also this series Vol. VIII
Knibbs and Palfreeman *Trans Faraday Soc.* 1921, 16, 402

⁵ Compare Oechslin *Zeitsch Elektrochem.* 1903, 9, 807 Bennett and Mack, *Trans Amer. Elektrochem Soc.* 1916, 29, 323

⁷ Knibbs and Palfreeman *loc. cit.*

⁸ Ries, *Zeitsch Kryst Min.* 1905, 41, 243

⁹ Carpenter *Chem and Met Eng.*, 1921, 24, 560

¹⁰ Le Chatelier *Bull Soc chim.* 1887, [2] 47, 300

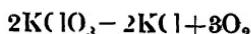
¹¹ Carnelley, *Trans Chem Soc.*, 1876, 29, 489

In the 9th Vol is a letter from Mr Gough, containing some animadversions, which were followed by an appropriate reply from Dr Henry

In the 8th, 9th, and 10th Volumes of Nicholson's Journal, and in the first Vol of the Manchester Memoirs (*new series*) may be seen some animadversions of Mr Gough, on my doctrine of mixed gases, with some of his own opinions on the same subject Mr Gough conceives the atmosphere to be a chemical compound of gases, vapour, &c and he rests his belief chiefly upon the observance of certain hygrometrical phenomena, such as that air absorbs moisture from bodies in certain cases, and in others restores it to them, shewing that air has an affinity for water, which may be overcome by another more powerful one This opinion, as Mr Murray observes, is the one we have from Dr Halley, it was supported by Le Roy, Hamilton and Franklin, and might be considered as the prevailing opinion, till Saussure, in his celebrated Essays on hygrometry, published in 1783, suggested that water was first changed into vapour, and was in that state dissolved by the air This amphibious theory of Saussure does not seem to have gained any converts to it, though it pointed out the instability of the other Finally, the theory

Scobai¹ has proved the reaction to take place in accordance with this equation by measuring the velocity of formation of potassium perchlorate at 395° C., and has also demonstrated its quadrinolecular nature.

² Simultaneously, a unimolecular reaction occurs, potassium chlorate decomposing with formation of potassium chloride, and evolution of oxygen



³ A sufficient rise in temperature initiates the decomposition of the potassium perchlorate, chiefly in accordance with the equation



and at 445° C there is complete decomposition in the sense indicated,² except for a small proportion of potassium chlorate simultaneously regenerated.³

The decomposition is much facilitated by the presence of certain oxides, such as manganese dioxide. The part played by these agents has been the subject of considerable controversy. Repeated use of the oxide produces no measurable diminution in its activity.⁴ The action has been suggested⁵ to be entirely mechanical, and analogous to that of sand and other substances in promoting the ebullition of water. On this assumption, all bodies in a fine state of division might be expected to exert a similar influence, a view at variance with the results of experiment. The oxides of metals capable of yielding more than one oxide, such as iron, nickel, copper, and cobalt, facilitate the reaction, but the oxides of zinc and magnesium are without effect. Probably higher and lower oxides of manganese are formed alternately at the expense of the chlorate.⁶ In presence of the oxide there is no apparent formation of potassium perchlorate,⁷ the manganese dioxide inducing the decomposition of the chlorate into chloride and oxygen at a temperature lower than that necessary for the autoxidation of the chlorate to perchlorate with appreciable velocity.⁸

Potassium perchlorate, KClO_4 —Careful heating of potassium chlorate causes partial autoxidation to perchlorate



The slight solubility of the perchlorate in dilute alcohol affords a means of separating it from the chloride. According to Blau and Weingland,⁹ the decomposition of the chlorate is best carried out in quartz flasks at 480° C without a catalyst, but when between 96 and 97 per cent of the chlorate has been transformed the perchlorate begins to decompose, so that the change is never complete. The decomposition of the perchlorate is much accelerated by the presence of traces of iron oxide,

¹ Scobai *Zeitsch physikal Chem* 1903 44 319

Frankland and Dingwall *Trans Chem Soc* 1887 51 279

² Feed *Proc Chem Soc*, 1885 1 105, 1886 2, 141 Frankland and Dingwall, *loc cit*

⁴ McLeod *Trans Chem Soc* 1889 55 184

⁵ Velye *Phil Trans* 1888 [A] 179 270

⁶ Sodeau *Trans Chem Soc* 1902 81 1066

⁷ Eccles, *J Chem Soc* 1876 29 857, Teed *Trans Chem Soc*, 1887, 51, 283

⁸ Sodeau *loc cit*, compare this series, Vol VII Part I

⁹ Blau and Weingland, *Zeitsch Elektrochem*, 1921, 27 1

	Feet
Sound moves in azotic gas	1000 per second
oxygen gas	930 —
carb acid	804 —
aqueous vap	1175 —

According to this table, if a strong and loud sound were produced 13 miles off, the first would be a weak impression of it brought by the atmosphere of aqueous vapour, in 59 seconds, the second would be the strongest of all, brought by the atmosphere of azotic gass, in $68\frac{1}{2}$ seconds, the third would be much inferior to the second, brought by the oxygenous atmosphere, in 74 seconds, the fourth and last brought by the carbonic acid atmosphere would be extremely weak in 85 seconds—Now though observation does not perfectly accord with the theory in this respect, it comes as near it, perhaps, as it does to that of the more simple constitution of the atmosphere which Mr Gough maintains Derham, who has perhaps made the greatest number of accurate observations on distant sounds, remarked that the report of a cannon fired at the distance of 13 miles from him, did not strike his ear with a single sound, but that it was repeated 5 or 6 times close to each other “ The two first cracks were louder than the

by the action of potassium hydroxide on perbromic acid, and forms crystals isomorphous with those of potassium perchlorate¹

Potassium hypoiodite, KOI—The hypoiodite has not been isolated, but is formed in aqueous solution by the interaction of iodine and a dilute solution of potassium hydroxide



The solution is employed in analysis as an oxidizer, the hypoiodite being reduced to iodide. It is unstable, one part of the hypoiodite undergoing oxidation at the expense of the remainder²



Potassium iodate, KIO₃—The iodate is formed by the oxidation of potassium iodide, either electrolytically, or by means of potassium permanganate or chlorate. The colourless, monoclinic³ crystals melt⁴ at 560° C, and have a density⁵ of 3.89. The heat of formation from the elements is given as 124.49 Cal⁶ and 126.1 Cal⁷. At 20° C the solubility is 8.1 grams per 100 grams of water, the boiling-point of the saturated solution being 102° C⁸. A semi-hydrate has been described⁹. On heating, potassium iodate decomposes with evolution of oxygen, the decomposition being facilitated by the presence of MnO₂.

When the iodate is crystallized from acid solution, a *di-iodate*, KIO₃.HIO₃, is formed¹⁰. It finds application in the determination of the concentration of hydrogen ions,¹¹ and also in volumetric analysis, since it reacts with potassium iodide and hydrochloric acid according to the equation



A *tri-iodate*, KIO₃.2HIO₃, has also been prepared¹⁰.

Potassium periodate, KIO₄—The periodate is produced by oxidizing a mixture of potassium iodate and hydroxide ether electrolytically or with chlorine. It crystallizes in quadratic pyramids, melting at 582° C,¹² and of density 3.618¹³ at 15° C. At 18° C its solubility is 0.66 gram per 100 grams water¹³. The heat of formation from the elements is 107.7 Cal¹⁴. In aqueous solution it is converted by potassium iodide into the iodate



From an aqueous solution of the periodate and potassium hydroxide a *basic periodate*, K₄I₂O₉.9H₂O, crystallizes.

Potassium manganate and permanganate—The methods of preparation and the properties of these are given in Vol. VIII.

¹ Kammerling *J. prakt. Chem.* 1863 90 190

Schweicker *Zeitsch. physikal. Chem.* 1895 16, 303

³ Ries *Zeutsch. Kryst. Min.* 1905, 41, 243

⁴ Carnelley and Williams *Trans. Chem. Soc.*, 1880 37 125

⁵ Clark *Amer. J. Sci.*, 1877 [3] 14 281

⁶ Thomsen *Thermochemistry* (Longmans 1908) 328

⁷ Berthelot *Ann. Chim. Phys.* 1878 [5] 13 27

⁸ Kremers *Pogg. Annalen* 1856 97 15

⁹ Ditte *Ann. Chim. Phys.* 1870 [4] 21 47

¹⁰ Moorburg *Chem. Weekblad* 1904 1 474

¹¹ Compare Sand *Ber.* 1906 39 2038

¹² Carnelley and Williams *Trans. Chem. Soc.* 1880 37 125

¹³ Barker *ibid.* 1908 93 15

¹⁴ Berthelot, *Thermocheimie Paris*, 1897 1 187

soon perceived it was necessary, if possible, to ascertain whether the atoms or ultimate particles of the different gases are of the same size or volume in like circumstances of temperature and pressure. By the size or volume of an ultimate particle, I mean in this place, the space it occupies in the state of a pure elastic fluid, in this sense the bulk of the particle signifies the bulk of the supposed impenetrable nucleus, together with that of its surrounding repulsive atmosphere of heat. At the time I formed the theory of mixed gases, I had a confused idea, as many have, I suppose, at this time, that the particles of elastic fluids are all of the same size, that a given volume of oxygenous gas contains just as many particles as the same volume of hydrogenous, or if not, that we had no data from which the question could be solved. But from a train of reasoning, similar to that exhibited at page 71, I became convinced that different gases have *not* their particles of the same size and that the following may be adopted as a maxim, till some reason appears to the contrary namely,—

That every species of pure elastic fluid has its particles globular and all of a size, but that no two species agree in the size of their

density¹ 2.044. The heat of formation from the elements is given as 102.76 Cal,² 103.2 Cal,³ and 104.6 Cal⁴, that from the monoxide and water as 49.72 Cal⁵. The latent heat of fusion per mol is 1.60 Cal.⁶ At 795° C the vapour-pressure is 8 mm.⁷

The solubility of potassium hydroxide has been studied by Pickering,⁸ some of his results being given in the appended table.

Solubility of Potassium Hydroxide.

Temperature, °C	-40	-30	-20	-10	0	10	20	30	40	50
Grams of KOH per 100 grams of water	61.2	82.4	87.9	92.3	99.2	106.1	112.7	122.2	136.9	143.9
Temperature, °C	60	70	80	90	100	110	120	130	140	
Grams of KOH per 100 grams of water	150	157.9	163.4	177.7	187.3	201.2	214.4	235.5	281.6	

The density of the solution saturated at 15° C is 1.536.

In chemical properties the potassium derivative resembles sodium hydroxide, the aqueous solution being a strong base,⁹ a solution containing 6.7 gram-molecules of the hydroxide per litre having the maximum OH' concentration.¹⁰ The hydroxide readily absorbs ozone, the product being possibly the heptoxide, K₂O₇,¹¹

Three hydrates have been isolated, the monohydrate, dihydrate, and tetrahydrate, melting respectively at 143° C, 35.5° C, and -82.7° C, the transition-point of the first and second being 32.5° C, and of the second and third -33° C.¹²

The action of aqueous solutions of potassium hydroxide on sulphur is similar to that of sodium hydroxide or of concentrated ammonium hydroxide (pp 111 and 220).

Potassium monosulphide, K₂S—The sulphide can be formed by direct union of the elements,¹³ by reduction of potassium sulphate with hydrogen or charcoal, and by the interaction of aqueous solutions of potassium hydroxide and potassium hydrogen sulphide. It is also produced by the action of sulphur on a solution of excess of potassium in liquid ammonia.¹⁴ On evaporation of its aqueous solution in vacuum at low temperature, the pentahydrate¹⁵ crystallizes. A dihydrate and a dodecahydrate are also known.¹⁶ The anhydrous salt can be obtained

¹ Filhol *Ann. Chim. Phys.* 1847, [3] 21, 415
de Forcrand *ibid.* 1908 [8] 15 433

² Ihomsen *Thermochemische Untersuchungen* Leipzig, 1882-1883 3 235

³ Berthelot, *Thermochimie* Paris, 1897, I 178

⁴ de Forcrand *loc. cit.*

⁵ Hevesy, *Zeitsch. physikal. Chem.* 1910, 73, 667

⁶ Jackson and J. J. Morgan *J. Ind. Eng. Chem.* 1921, 13, 110

⁷ Pickering, *Trans. Chem. Soc.*, 1893, 63 908

⁸ On the heat of neutralization by hydrochloric acid, hydrobromic acid, hydriodic acid and nitric acid compare Richards and Rowe, *J. Amer. Chem. Soc.*, 1922, 44 684

⁹ Kohlhausch, *Wied. Annalen* 1879, 6, 1, 145

¹⁰ Traube *Bei.* 1912 45 2201

¹¹ Pickering *Trans. Chem. Soc.*, 1893, 63 908

¹² Rengade and Costeanu, *Compt. rend.*, 1913, 156 791

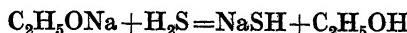
¹³ Hugot, *ibid.*, 1899, 129, 388

¹⁴ Schone, *Pogg. Annalen*, 1867 131, 380

¹⁵ Bloxam, *Trans. Chem. Soc.*, 1900 77, 753, Sabatier, *Ann. Chim. Phys.* 1881, [5]

being 45° above the horizontal plane, or that plane which passes through the centres of the four particles. On this account the pressure is steady and uniform throughout. But when a measure of one gas is presented to a measure of another in any vessel, we have then a surface of elastic globular particles of one size in contact with an equal surface of particles of another in such case the points of contact of the heterogeneous particles must vary all the way from 40° to 90° , an intestine motion must arise from this inequality, and the particles of one kind be propelled amongst those of the other. The same cause which prevented the two elastic surfaces from maintaining an equilibrium, will always subsist, the particles of one kind being from their size unable to apply properly to the other, so that no equilibrium can ever take place amongst the heterogeneous particles. The intestine motion must therefore continue till the particles arrive at the opposite surface of the vessel against any point of which they can rest with stability, and the equilibrium at length is acquired when each gas is uniformly diffused through the other. In the open atmosphere no equilibrium can take place in such case till the particles have ascended so far as to be restrained by their own weight,

aqueous solution of potassium hydroxide with hydrogen sulphide,¹ evaporating to dryness in vacuum, and eliminating the water from the resulting $\frac{1}{4}$ -hydrate² or $\frac{1}{2}$ -hydrate³ by a current of dry hydrogen. It can be precipitated quantitatively by adding benzene or ether to a solution of sodium ethoxide in absolute alcohol saturated with hydrogen sulphide.⁴



Potassium hydrogen sulphide forms white, microscopic cubes, more deliquescent than the corresponding sodium derivative. The heat of formation from the element is given as 64.0 Cal,⁵ and that in aqueous solution as 65.1 Cal.⁶

Potassium sulphite, K_2SO_3 .—The sulphite can be prepared by passing sulphur dioxide into a solution of potassium carbonate till evolution of carbon dioxide ceases, or by dissolving a known weight of potassium hydroxide in water, saturating with sulphur dioxide, and adding an equal weight of the hydroxide. Evaporation of the solution yields the rhombic *dihydrate*, which is transformed into the anhydrous salt at 120° C., a white solid with heat of formation 272.6 Cal.⁷ A *mono-hydrate* is also known.

Potassium hydrogen sulphite, KHSO_3 .—The primary sulphite can be precipitated in monoclinic crystals by addition of alcohol to a solution of potassium carbonate into which excess of sulphur dioxide has been passed. It is unstable, readily losing sulphur dioxide. Its heat of formation in aqueous solution is 211.3 Cal.⁸

Potassium pyrosulphite, $\text{K}_2\text{S}_2\text{O}_5$.—On treatment of a hot saturated solution of potassium carbonate with sulphur dioxide, the pyrosulphite separates in monoclinic crystals, which are more stable than those of the primary sulphite. Its heat of formation from the elements is 369.4 Cal.⁸ It is employed in the preparation of photographic developers under the name "potassium metabisulphite."

Potassium sulphate, K_2SO_4 .—The sulphate occurs in nature in the form of double salts. Examples are *schonite*, $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, *polyhalite*, $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and *glaserite*, $3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$. It is a by product in the manufacture of nitric acid from potassium nitrate and sulphuric acid, and can also be prepared by the action of sulphuric acid on potassium chloride. The main sources of potassium sulphate are *kainite* ($\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$) and *sylvine* (KCl), both present in the Stassfurt "Abraumsalze". Water decomposes kainite into a sparingly soluble double sulphate of potassium and magnesium, and the very soluble magnesium chloride; a similar product is obtained by the interaction of sylvine and *kiescrite* ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$). The magnesium chloride is removed by cold water, and the residual double sulphate treated with excess of an aqueous solution of potassium chloride.



¹ Compare Biltz and Wilke Dorfert *Ber.*, 1905, 38, 125.

² Schone *Pogg Annalen* 1867, 131, 380.

³ Bloxam *Trans Chem Soc.*, 1900, 77, 753.

⁴ Rule *ibid.* 1911, 99, 558.

⁵ Sabatier *Ann Chim Phys.* 1881, [5] 22, 22.

⁶ Thomsen, *Pogg Annalen* 1870, 139, 242.

⁷ Berthelot, *Ann Chim Phys.* 1884, [6] 1, 76.

⁸ Berthelot, *ibid.*, 87.

liquid, is precisely the same as if it were the only gas present occupying the whole space, and all the rest were withdrawn

In other respects I think the last view accords better with the phenomena, and obviates the objections which Dr Thomson has brought against the former, particularly in regard to the query, why mixed gases that are known on certain occasions to combine, do not always combine, and why any gaseous particle in its nascent state is more disposed to combination than when it has already assumed the elastic form It will also more clearly explain the reason of one gas making so powerful and durable a resistance to the entrance of another

One difficulty still remains respecting vapour, which neither view of the subject altogether removes though vapour may subsist in the atmosphere upon either supposition, as far as the temperature will admit, not being subject to any more pressure than would arise from its own particles, were the others removed, yet it may be enquired, how does it rise from the surface of water subject to the pressure of the atmosphere? how does vapour which ascends with an elastic force of only half an inch of mercury, detach itself from water when it has the weight of 30 inches of mercury to oppose its ascent? This difficulty

Potassium hydrogen sulphate is dimorphous, crystallizing in the rhombic and also in the monoclinic system. Its melting-point is given as 200° C¹ and 210° C² and its mean density as 2.355³. The heat of formation from the elements is recorded as 276.1 Cal⁴ and 277.1 Cal⁵.

The solubility in water is given in the table

Solubility of Potassium Hydrogen Sulphate

Temperature, °C	0	20	40	100
Grams of KHSO ₄ in 100 grams of water	36.8	51.4	67.8	121.6

The boiling-point of a solution in contact with excess of salt is 108° C⁶. The solution has a very acidic reaction. On heating above the melting-point it is converted into the pyrosulphate.

Several other potassium hydrogen sulphates have been described⁷. Examples of such compounds are K₂SO₄.3H₂SO₄ with melting-point 91.5° C, and K₂SO₄.H₂SO₄ with melting-point 218.6° C⁸.

Potassium pyrosulphate, K₂S₂O₇.—The pyrosulphate is produced by heating potassium hydrogen sulphate, or by the action of sulphur trioxide on the normal sulphate. It forms colourless crystals, melting⁹ above 300° C, and of density 2.277. The heat of formation is 474.2 Cal¹⁰.

Potassium persulphate, K₂S₂O₈.—The persulphate is formed in the electrolysis of the primary sulphate or normal sulphate in concentrated solution,¹¹ with a current density of 5 amperes per sq cm. The use of a diaphragm is unnecessary, and the yield is much higher when the electrolyte contains hydrofluoric acid. The compound is also manufactured by double decomposition from ammonium persulphate. Any excess of this salt can be eliminated¹² by crystallizing from hot water in presence of sufficient barium hydroxide to decompose the ammonium derivative. The heat of formation of potassium persulphate is 454.5 Cal,¹³ and the solubility at 0° C is 1.76 grams per 100 grams of water.¹⁴ With concentrated sulphuric acid it forms complex derivatives containing a large proportion of oxygen.¹⁵ It unites with hydrogen peroxide to form an unstable compound, probably having the formula K₂S₂O₈.H₂O₂. This substance decomposes spontaneously into potassium hydrogen sulphate and oxygen.¹⁶ Although it has no action on a

¹ Mitscherlich *Pogg Annalen* 1830 18 152 173

² Schultz Sellack *Jahresber* 1871 217

³ Compare Schroder *Dichtigkeitsmessungen* Heidelberg 1873 Clarke, *Constants of Nature* 2nd ed Washington 1888 1 89

⁴ Berthelot *Ann Chim Phys* 1873 [4] 29 435

⁵ Thomsen *Thermochemische Untersuchungen* Leipzig, 1882-1883 3 236

⁶ Kremers *Pogg Annalen* 1856, 97 15

⁷ Stortenbeker *Rec trav chim* 1902 21 401 van Bemmelen *Festschrift* 1910 329
d Ans *Zeitsch anorg Chem* 1909, 63 225, 1913 80 295 Beigius *Zeitsch physikal Chem* 1910 72 338 Aizalier *Compt rend* 1908 147 129

⁸ Kendall and Landon *J Amer Chem Soc* 1920 42 2131

⁹ Schultz Sellack *Jahresber* 1871 217

¹⁰ Berthelot *Ann Chim Phys*, 1873 [4] 30 442

¹¹ Marshall *Trans Chem Soc* 1891 59 771

¹² Mackenzie and Marshall *ibid* 1908 93 1726

¹³ Berthelot *Ann Chim Phys*, 1892 [6] 26 538 550

¹⁴ Marshall *Trans Chem Soc* 1891, 59 772

¹⁵ Compare this series, Vol VII

¹⁶ Friend, *Trans Chem Soc*, 1906, 89, 1092

SECTION 3

ON THE

CONSTITUTION OF LIQUIDS,

*And the Mechanical Relations betwixt Liquids
and Elastic Fluids*

A liquid or inelastic fluid may be defined to be a body, the parts of which yield to a very small impression, and are easily moved one upon another This definition may suffice for the consideration of liquids in an hydrostatical sense, but not in a chemical sense Strictly speaking, there is no substance inelastic, if heat be the cause of elasticity, all bodies containing it must necessarily be elastic but we commonly apply the word elastic to such fluids only as have the property of condensation in a very conspicuous degree Water is a liquid or inelastic fluid, but if it is compressed by a great force, it yields a little, and again recovers its original bulk when the pressure is removed We are indebted to Mr Canton for a set of experiments by which the compressibility of several liquids is demonstrated Water, he found, lost about

yield the anhydrous salt in the form of very stable white crystals,¹ also produced by the interaction of sulphur dioxide and potassium hydride²

Potassium selenides—The *monoselenide*, K₂Se, is formed by the action of selenium on excess of potassium dissolved in liquid ammonia, with excess of selenium the *tetraselenide*, K₂Se₄, is produced³. Each compound resembles the corresponding sodium derivative. With solutions of potassium carbonate, hydrogen selenide reacts forming a number of hydrates of the monoselenide. The heat of formation of the anhydrous mono-derivative is given as 79.4 Cal.⁴ The *triselenide* has been isolated,⁵ and Fabre has also described the *primary selenide*, KSeH.

Potassium selenites—Little is known of the selenites, but a *normal selenite*, a *primary selenite*, and a *pyroselenite* have been described.⁶

Potassium selenate, K₂SeO₄—Electrolytic oxidation of the solution of selenite formed by the interaction of selenious acid and potassium carbonate yields potassium selenate,⁷ rhombic crystals⁸ of density⁹ 3.066 at 20° C. At the same temperature its solubility is 111 grams per 100 grams of water.¹⁰ Electrolytic oxidation of its solution acidified with selenic acid converts the selenate into *potassium perselenate*.¹¹

Potassium tellurides—The *monotelluride*, K₂Te, was originally produced by Davy¹² by direct combination of the elements. At 250° C the reaction is even more energetic than that between sodium and tellurium. When prepared in an atmosphere of hydrogen, the product has a crystalline structure, and a dark iridescent-purple colour. With water it yields a purple solution, being reprecipitated by alcohol in the form of small, ill defined crystals.¹³

The monotelluride and the *tritelluride*, K₂Te₃, have been prepared by the interaction of tellurium and a solution of potassium in liquid ammonia.¹⁴

Potassium tellurate,¹⁵ K₂TeO₄—At 20° C the solubility of the tellurate is 27.53 grams per 100 grams of water.¹⁶

Potassium chromates—The modes of preparation and an account of the properties of potassium chromate and dichromate are given in Volume VII.

Potassium nitride, K₃N—The nitride is said¹⁷ to be formed by heating potassamide, but the statement has not been confirmed by the

¹ Bazlen Ber 1905 38 1057 German Patent No 119676
Moissan Compt rend 1902 135 647

² Hugot ibid 1899 129 299

³ Fabre Ann Chim Phys 1887 [6], 10 506

Clever and Muthmann Zeitsch anorg Chem 1895 10 117

⁴ Compte Muthmann and Schaefer Ber 1893 26 1014

⁵ Muller Ber 1903 36 4262

⁶ For isomorphism see p 227

⁷ Tutton Trans Chem Soc 1897 71 846

⁸ Etard Ann Chim Phys 1894 [7] 2 550 compare Tutton loc cit

⁹ Dennis and Brown J Amer Chem Soc 1901 23 358

¹⁰ Davy Phil Trans 1810 27 16

¹¹ Gibbs J Amer Chem Soc 1909 31 902

¹² Hugot Compt rend 1899 129 388

¹³ On potassium tellurite, compare Lenher and Wolensky, J Amer Chem Soc 1913

¹⁴ 718

¹⁵ Rosenheim and Weinheber, Zeitsch anorg Chem 1911 69 261

¹⁶ Gray Lussac and Thénard Recherches physico chimiques 1811, I 337 Davy Phil Trans 1809 40 150

even here we perceive the attractive force to prevail, there being a manifest cohesion of the particles Whence does this arise? It should seem that when two particles of steam coalesce to form water, they take their station so as to effect a perfect equilibrium between the two opposite powers, but if any foreign force intervene, so as to separate the two molecules an evanescent space, the repulsion decreases faster than the attraction, and consequently this last acquires a superiority or excess, which the foreign force has to overcome If this were not the case, why do they at first, or upon the formation of water, pass from the greater to the less distance?

With regard to the collocation and arrangement of particles in an aggregate of water or any other liquid, I have already observed (page 139) that this is not, in all probability, the same as in air It seems highly improbable from the phenomena of the expansion of liquids by heat The law of expansion is unaccountable for, if we confine liquids to one and the same arrangement of their ultimate particles in all temperatures, for, we cannot avoid concluding, if that were the case, the expansion would go on in a progressive way with the heat, like as in air, and there

nitrogen. If the mixed gases are passed through a solution of an alkali-metal hydroxide, pure nitric oxide is isolated. For laboratory purposes this method affords a convenient means of preparing the gas, 10 grams of potassium nitrite producing about 25 litres of the oxide.

Potassium nitrate, KNO_3 .—The nitrate is manufactured from natural saltpetre earths found in Bengal, and to a less extent in Egypt and elsewhere. The nitrate in these earths is produced by the oxidation of organic matter by the action of "nitrifying" bacteria in presence of atmospheric oxygen, a warm, moist climate being particularly favourable for the process. The nitrate is extracted by lixiviating the earth in vessels of earthenware or wood, and concentrating the aqueous solution in iron pots by solar or artificial heat.

Artificial saltpetre earths can be prepared by allowing stable refuse to nitrify in contact with a porous soil containing calcium carbonate, the nitrate being isolated by lixiviation and purified by crystallization. The salt is also manufactured from sodium nitrate by the action of potassium chloride, since it crystallizes out from a hot concentrated solution of these two substances as the temperature falls. When prepared from Chile saltpetre, it often contains sodium nitrate, and chloride, chlorate, and perchlorate of potassium.

The extraordinary demand for nitric acid and nitrates brought about by the abnormal conditions consequent on the great European War of 1914 and succeeding years gave a powerful impetus to the development of synthetic methods for the fixation of atmospheric nitrogen. For an account of these developments reference should be made to Volume VI of this series.

At ordinary temperature, potassium nitrate crystallizes in the rhombic system, at higher temperatures the crystals formed are rhombohedral. The transition-point is $129.5^\circ C^1$. The second form is said² to exist in two modifications, α and β . Among the values given for the melting point are $338^\circ C^3$, $334.5^\circ C^4$ and $339^\circ C^5$, for that of the rhombohedral form $334^\circ C^6$. For the density the mean value is given as 2.092^7 , other determinations giving 2.1047^8 , 2.109^9 at $16^\circ C$, 2.109^{10} at $20^\circ C$, and $2.014 - 0.0006t^{11}$ at temperatures ranging from 350° to $500^\circ C$. The heat of formation from the elements is given as 119 Cal^{12} and 119.5 Cal^{13} . The molecular electric conductivity of potassium nitrate between 346.1° and $500.4^\circ C$ is given by the formula¹⁴

$$\mu_t = 36.21 + 0.1875(t - 350)$$

¹ van Fyck *Zeitsch physikal Chem* 1905 51 721

Wallrant *Compt rend* 1905 140 264 1906 142 100 168

³ Lorenz Frei and Jabs *Zeitsch physikal Chem* 1908 61 468

⁴ Stein *ibid* 1909 65 667 Hugh *J Amer Chem Soc* 1912 34 1137

van Fyck loc cit Person *Ann Chim Phys* 1847 [3] 21 295 Cunelley *Trans Chem Soc* 1878 33 273

⁶ Rozsboom *Proc K Akad Wetensch Amsterdam* 1902 4, 374

⁷ Compte Clark's *Constants of Nature* 2nd ed., Washington 1888 1 109 and 110

⁸ Andriæc *Zeitsch physikal Chem* 1913, 82, 109

⁹ Retgers *ibid* 1889 3 289

¹⁰ Haigh loc cit

¹¹ Lorenz Frei and Jabs loc cit

¹² Berthelot *Thermochimie* Paris 1897 1 193

¹³ Thomsen *Thermochemical Untersuchungen* Leipsic, 1882-1883 3 236

¹⁴ Jaeger and Kapma, *Zeitsch anorg Chem*, 1920, 113, 27

ware, or gases, in regard to their power of confining elastic fluids? Do they treat all gases alike, or do they confine some, and transmit others? These are important questions, they are not to be answered in a moment We must patiently examine the facts

Before we can proceed, it will be necessary to lay down a rule, if possible, by which to distinguish the *chemical* from the *mechanical* action of a liquid upon an elastic fluid I think the following cannot well be objected to *When an elastic fluid is kept in contact with a liquid, if any change is perceived, either in the elasticity or any other property of the elastic fluid, so far the mutual action must be pronounced CHEMICAL but if no change is perceived, either in the elasticity or any other property of the elastic fluid, then the mutual action of the two must be pronounced wholly MECHANICAL*

If a quantity of lime be kept in water and agitated, upon standing a sufficient time, the lime falls down, and leaves the water transparent but the water takes a small portion of the lime which it permanently retains contrary to the Laws of specific gravity Why? Because that portion of lime is dissolved by the water If a quantity of air be put to water

Potassium phosphides—Phosphine reacts with a solution of potassium in liquefied ammonia to form *potassium dihydroposphide*, KH_2P , white crystals decomposed by moist air with evolution of phosphine¹. On heating, it is converted into *tripotassium phosphate*, K_3P . A solution of potassium in liquefied ammonia reacts with red phosphorus to form *potassium pentaphosphide*, KP_5 ². The black product formed from potassium and phosphorus loses its excess of metal in vacuum at 400° to 450° C, yielding *dipotassium pentaphosphide*, K_2P_5 . It is a lemon-yellow substance with a density of about 2, is unstable in air, and is decomposed by water with formation of solid phosphorus hydride³.

Potassium hypophosphate, KH_2PO_2 —The hypophosphate is formed by the action of phosphorus on alcoholic potash. It resembles the corresponding sodium derivative.

Potassium phosphites and hypophosphates—*Monopotassium* and *dipotassium hydrogen phosphate*, *potassium pyrophosphate*, and *potassium hypophosphate* are obtained by methods analogous to those employed for the corresponding sodium salts.

Potassium orthophosphates—The normal salt, *potassium orthophosphate*, K_3PO_4 , is obtained by heating basic slag or native calcium phosphate with charcoal and potassium sulphate. The potassium sulphide simultaneously formed is converted into phosphate by addition of phosphoric acid, or the potassium phosphate is precipitated by addition of alcohol. The aqueous solution of the salt is very alkaline in reaction, owing to hydrolytic dissociation. The heat of formation from the elements in solution is 483.6 Cal⁴.

The interaction of the calculated quantities of phosphoric acid and potassium carbonate in aqueous solution yields *dipotassium hydrogen phosphate*, K_2HPO_4 . It is only known in solution, and in this form has a slightly alkaline reaction to litmus, but is neutral to phenolphthalein. Its heat of formation in aqueous solution is 429.2 Cal⁴.

Calcium phosphate reacts with potassium hydrogen sulphate and sulphuric acid to form *potassium dihydrogen phosphate*, KH_2PO_4 , the most important of the potassium phosphates. It forms doubly refracting crystals melting at 96° C., of density 2.3325⁶ at 9.2° C., and 2.338⁷ at 20° C., and of specific heat 0.208 between 17° and 48° C.⁸ The heat of formation in aqueous solution is 374.4 Cal⁹. When heated at 244° C., it loses water, yielding the acid pyrophosphate, $\text{K}_2\text{H}_2\text{P}_2\text{O}_7$,¹⁰

Potassium pyrophosphate, $\text{K}_4\text{P}_2\text{O}_7$ —The pyrophosphate is produced by heating dipotassium hydrogen phosphate, or by neutralizing anhydrous phosphoric acid with potassium hydroxide dissolved in absolute alcohol. Its specific heat is 0.1910 between 17° and 98° C.¹¹ It is soluble in water, forming a slightly alkaline solution, and yields a trihydrate.

Potassium metaphosphates—In mode of formation and character the

¹ Joannis *Compt rend* 1894 119, 557

Hugot *ibid* 1895, 121 206

³ Hackspill and Bossuet *ibid* 1912 154 209

⁴ Berthelot *Thermochimie* Paris, 1897 i 193

Tilden *Trans Chem Soc* 1884 45 266

⁶ Muthmann *Zeitsch Kryst Min* 1894 22 497

⁷ Kuckmyer *Zeitsch physikal Chem* 1896 21, 53

⁸ Kopp, *Annalen Suppl*, 1864-5, 3, 1, 289

⁹ Berthelot *loc cit*

¹⁰ Balaieff, *Zeitsch anorg Chem* 1921 118 123

¹¹ Regnault, *Pogg Annalen*, 1841, 53, 60 243

to be retained by the attraction of the water; in the second case, the water seemed indifferent; in the third, it appears as if repulsive to the air, yet in all three, it is the same air that has to act on the same water. From these facts, there seems reason then for maintaining three opinions on the subject of the mutual action of air and water, namely, that water attracts air, that water does not attract it, and that water repels air. One of these must be true, but we must not decide hastily. Dr Priestley once imagined, that the clay of a porous earthen retort, when red hot, "destroys for a time the aerial form of whatever air is exposed to the outside of it, which aerial form it recovers, after it has been transmitted in combination from one part of the clay to another, till it has reached the inside of the retort." But he soon discarded so extravagant an opinion.

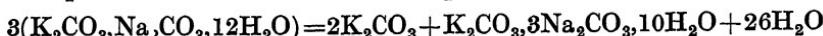
From the recent experiments of Dr Henry, with those of my own, there appears reason to conclude, that a given volume of water absorbs the following parts of its bulk of the several gases

Potassium carbonate is also manufactured from the spent wash of the spirit-distiller, and from the residual liquor of the wool-scourer

Potassium carbonate is a white solid. Its melting-point is given by various experimenters as 878.6° C,¹ 880° C,² 885° C,³ 873.1° C,⁴ 887.5° C,⁵ 891° C,⁶ 894° C,⁷ 897.3° C,⁸ 897.7° C,⁹ 900° C.¹⁰ For the density the mean value is given⁸ as 2.29, a more recent determination⁹ gives 2.3312 at 17° C. Its specific heat is 0.206 between 17° and 47° C,¹¹ and 0.2162 between 23° and 99° C.¹² At 970° C the vapour-pressure is 1.68 mm, and at 1130° C it is 5.0 mm.¹³ The heat of formation from the elements is recorded as 275.87 Cal,¹⁴ 278.8 Cal,¹⁵ and 281.1 Cal.¹⁶ Potassium carbonate exhibits diamagnetism.

Several hydrates have been described, but their constitutions are not definitely settled.¹⁶ At 25° C the solubility is 113.5 grams per 100 grams of water,¹⁶ and at 130° C it is 196 grams.¹⁷ The aqueous solution has a strong alkaline reaction, due to hydrolytic dissociation. It forms various primary carbonates by interaction with atmospheric carbon dioxide,¹⁸ and unites with hydrogen peroxide yielding compounds of the formulæ K₂CO₃.3H₂O₂ and K₂CO₃.2H₂O₂.½H₂O.¹⁹

Potassium sodium carbonate, K₂CO₃.Na₂CO₃.12H₂O — A double salt of this formula is a constituent of vegetable ashes. At 35° C it decomposes in accordance with the equation



The double carbonate thus generated decomposes at a temperature of about 180° C.²⁰

Potassium hydrogen carbonate, KHCO₃ — Carbon dioxide precipitates the primary carbonate from a concentrated solution of potassium carbonate in the form of monoclinic crystals of density²¹ 2.17. The heat of formation from the elements is given as 231.68 Cal²² and 233.3 Cal.²³ In dilute aqueous solution it has an alkaline reaction, owing to hydrolytic dissociation in accordance with the equation



¹ Victor Meyer Riddle and Lamb *Ber*, 1893, 26, 3129

² Ramsay and Eumorfopoulos, *Phil Mag* 1896, 41, 360

³ Le Chatelier *Bull Soc chim* 1887 [2] 47, 300

⁴ Niggli *J Amer Chem Soc* 1913 35, 1693

⁵ Huttner and Iammann *Zeitsch anorg Chem*, 1905 43, 215

⁶ McCrae, *Wied Annalen* 1895 55, 95

⁷ Aindt *Zeitsch Elektrochem*, 1906 12, 337

⁸ Compare Clarke *Constants of Nature*, 2nd ed Washington 1888 1 126 Schroeder *Dichtigkeitsmessungen*, Heidelberg, 1873

⁹ East of Berkley *Proc Chem Soc* 1906 22, 321

¹⁰ Kopp *Annalen Suppl* 1864-5 3 1 289

¹¹ Regnault *Pogg Annalen* 1841 53 60, 243

¹² Jackson and J J Morgan *J Ind Eng Chem*, 1921 13, 110

¹³ de Forcand *Compt rend*, 1909 149, 719

¹⁴ Berthelot, *Ann Chim Phys* 1875 [5] 4 111

¹⁵ Thomsen *Thermochemische Untersuchungen I* Cipsic, 1882-1883 3 230

¹⁶ Meyerhoff *Landolt, Bornstein, and Meyerhoff's Tabellen* 3rd ed, Berlin 1905, 542

¹⁷ Mulder *Scheikunde* Rotterdam 1864 97

¹⁸ de Forcand *Compt rend* 1909 149, 719 825

¹⁹ Kazanetsky *J Russ Phys Chem Soc* 1902 34, 388

²⁰ Bain and Oliver *Trans Roy Soc Canada* 1916 [3] 10 65

²¹ Compare Clarke, *Constants of Nature*, 2nd ed, Washington, 1888 1 129 Schroeder *Dichtigkeitsmessungen* Heidelberg 1873

²² de Forcand *loc cit*

²³ Berthelot, *loc cit*

circumstances, the experiments of Dr Henry have decided this point, by ascertaining, that if the exterior gas is condensed or rarefied in any degree, the gas absorbed is condensed or rarefied in the same degree, so that the proportions absorbed given above are absolute

One remarkable fact, which has been hinted at is, that no one gas is capable of retaining another in water, it escapes, not indeed instantly, like as in a vacuum, but gradually, like as carbonic acid escapes into the atmosphere from the bottom of a cavity communicating with it

It remains now to decide whether the relation between water and the abovementioned gases is of a *chemical* or *mechanical* nature. From the facts just stated, it appears evident that the elasticity of carbonic acid and the other two gases of the first class is not at all affected by the water. It remains exactly of the same energy whether the water is present or absent. All the other properties of those gases continue just the same, as far as I know, whether they are alone or blended with water. We must therefore, I conceive, if we abide by the Law just laid down, pronounce the mutual action between these gases and water to be *mechanical*.

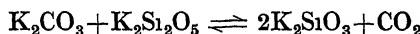
A very curious and instructive phenomenon

ferrocyanide and potassium carbonate with the same reagent. The colourless, deliquescent crystals melt¹ at 161.2° or 172.3° C., their density being 1.886.² At 430° C the salt develops a blue colour, but becomes white again on cooling. The heat of formation from the elements is 50.5 Cal,³ and at 20° C the solubility⁴ is 21.7 grams per 100 grams of water. Sulphur dioxide reacts with it in aqueous solution to form a complex derivative.⁵ Sodium hypobromite reacts energetically with potassium thiocyanate, evolving heat and forming potassium cyanate and sulphate.⁶

Potassium ferrocyanide and ferricyanide—The modes of preparation and the properties of potassium ferrocyanide, of potassium ferricyanide, and of similar salts are described in Vol. IX, Part II.

Potassium silicates—Potash water-glass is prepared similarly to the corresponding sodium product. When the calculated proportion of potassium hydroxide and silicic acid is employed, addition of alcohol to the solution precipitates *potassium metasilicate*, K₂SiO₃. When kept for a prolonged period over sulphuric acid, the syrup-like potash water-glass deposits hygroscopic plates, probably K₄SiO₄.2KOH.8H₂O.⁷

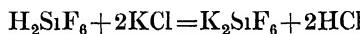
Niggli⁸ has demonstrated that on fusion of potassium carbonate and silica an equilibrium between the disilicate (see below) formed and the carbonate is attained



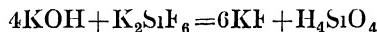
With rise of temperature the proportion of metasilicate increases.

By heating mixtures of water and finely powdered glasses at high temperatures, Morey and Fenner⁹ have prepared *potassium hydrogen disilicate*, KHSi₂O₅, in the form of orthorhombic crystals which do not lose water even at 350° C., and *potassium disilicate*, K₂Si₂O₅, a hygroscopic salt readily acted upon by water, and melting at 1015° ± 10° C.⁸

Potassium fluosilicate, K₂SiF₆—The fluosilicate is precipitated in the form of microscopic crystals of slight solubility by the action of fluosilicic acid on solutions of potassium salts



It is decomposed by alkali metal hydroxides with formation of a fluoride and silicic acid, and can be estimated by this method with phenolphthalein as indicator



Potassium hypoborate, KH₃OB—The hypoborate is a very deli-

¹ Pohl, *Sitzungsber. A Akad. Wiss. Wien*, 1851, 6, 587. Paterini and Mazzucchelli, *Atti R. Accad. Lincei*, 1907, [5], 16, 1 465.

Bodicker, *Jahresber.*, 1860 17.

² Joannis, *Ann. Chem. Phys.*, 1882 [5] 26 482.

³ Rudolf Pogg, *Annalen* 1872, 145 611, compare H. W. Foote, *Amer. Chem. J.* 1903, 30, 330.

Walden, *Ber.* 1899, 32 2862, Iox, *Zeitsch. physikal. Chem.* 1902, 41 458. Walden and Contcniszwei, *ibid.* 1903, 42 456. Smits, *ibid.*, 1905, 51 193.

⁴ Dehn, *J. Amer. Chem. Soc.* 1909, 31 1220.

⁵ Jordis, *Zeitsch. anorg. Chem.* 1908, 58 98.

⁶ Niggli, *J. Amer. Chem. Soc.* 1913, 35 1693.

⁷ Morey and Fenner, *ibid.*, 1914, 36 215.

whatever does it appear that the elasticity of any of these gases is affected, if water takes $\frac{1}{7}$ of its bulk of any gas, the gas so absorbed, exerts $\frac{1}{7}$ of the elasticity, that the exterior gas does, and of course it escapes from the water when the pressure is withdrawn from its surface, or when a foreign one is induced, against which it is not a proper match. As far as is known too, all the other properties of the gases continue the same, thus, if water containing oxygenous gas be admitted to nitrous gas, the union of the two gases is certain, after which the water takes up $\frac{1}{7}$ of its bulk of nitrous gas, as it would have done, if this circumstance had not occurred. It seems clear then that the relation is a mechanical one *

* Dr Thomson and Mr Murray have both written largely in defence of the notion that *all* gases are combined with water, that a real union by means of a chemical affinity which water exercises in a greater or less degree towards all gases, takes place, this affinity is supposed to be of the *slight* kind, or of that kind which holds all gases in a state of solution, one amongst another, without any distinction. The opposite doctrine was first stated in a paper of mine, on the absorption of gases by water (Manch Memoirs, new series, Vol 1) Previously to the publication of that paper, Dr Henry, who was convinced from his own experience, that the connection of gases with water was of a mechanical nature, wrote two essays in

The test serves to identify potassium in presence of sodium. The metal is detected and estimated quantitatively by precipitation with chloroplatinic acid as potassium chloroplatinate, K_2PtCl_6 , or by conversion into perchlorate. The insolubility of these salts in alcohol facilitates the separation of potassium from sodium.¹ Acetone has the advantage of dissolving both chloroplatinic acid and sodium chloroplatinate, but not the potassium salt.² The metal is also estimated as sulphate, chloride, primary tartrate,³ and cobaltinitrite.⁴

¹ Morozewicz, *Bull Acad Sci Cracow*, 1906, 796

² Meillère, *J Pharm Chim*, 1913, [7], 7, 281

³ Compare Marshall, *Chem Zeit*, 1914, 38, 585, 615

⁴ Compare Mitscherlich and Fischer, *Landw Versuchs Stat*, 1912, 78, 75, van den Bos, *Chem Weekblad* 1913, 10, 182, McDougall, *J Amer Chem Soc* 1912, 34, 1684, Burgess and Kamm, *ibid*, 652, Zaleski, *Landw Versuchs Stat*, 1913, 83, 221. On the separation of potassium from rubidium and caesium, compare Wernadski, *Bull Soc franç Min*, 1913, 36, 258

butes to support the incumbent atmosphere Finally, the gas gets completely diffused through the water, so as to be of the same density within as without, the gas within the water then presses on the containing vessel only, and reacts upon the incumbent gas The water then sustains no pressure either from the gas within or without In olefiant gas the surface of the water supports $\frac{7}{8}$ of the pressure, in oxygenous, &c $\frac{2}{3} \frac{6}{7}$, and in hydrogenous, &c $\frac{6}{5} \frac{3}{4}$

When any gas is confined in a vessel over

mechanical, and those where the exertion of affinity must be allowed to operate" I conceive nothing is more easy than to point out the exact line of distinction wherever water is found to diminish or destroy the elasticity of any gas, it is a chemical agent, wherever it does neither of these, it is a mechanical agent Whoever undertakes to maintain the chemical theory of the absorption of gases by water, should in the outset over turn the following argument preferred by Dr Henry "The quantity of every gas, absorbed by water, follows exactly the ratio of the pressure, and since it is a rule in philosophizing, that effects of the same kind, though differing in degree, are produced by the same cause, it is perfectly safe to conclude, that every, even the minutest portion of any gas, in a state of absorption by water, is retained entirely by incumbent pressure There is no occasion, therefore, to call in the aid of the law of chemical affinity, when a mechanical law fully and satisfactorily explains the appearances"

0 3 Its melting point is given as 37° C,¹ 37.8° C,² 38° C,³ 38.5° C,⁴ and 39° C,⁵ and its boiling-point as 696° C at 760 mm pressure,⁶ the vapour being greenish-blue in colour. At 180° C the vapour has a purple-red colour, which changes to orange above 350° C.⁷ Its density is given as 1.52 (Bunsen and Kirchhoff⁸), 1.5248 at 0° C (Hackspill⁹), 1.522 at 15° C (Erdmann and Kothner¹⁰), and 1.532 at 20° C (Richards and Brink¹¹). The table on p. 2 indicates that in melting point and density rubidium and caesium are more closely related to one another than to the other alkali-metals, and a similar resemblance has been observed regarding the crystallography of the salts of the two metals.¹² According to Rengade,¹³ the specific heat of the solid at its melting-point is 0.019, and the heat of fusion per gram is 0.00615 Cal.

Several rubidium salts exhibit radioactivity,¹⁴ among them the sulphate,¹⁵ chloride, and chlorate.¹⁶ The action of the sulphate on the photographic plate is more powerful than that of potassium sulphate.¹⁷

Chemical Properties — In its chemical character rubidium occupies a position intermediate between potassium and caesium. It combines with atmospheric oxygen and decomposes water more energetically than potassium, and the bright metal ignites spontaneously in dry oxygen. It begins to react with ice at -108° C.¹⁸ When dissolved in liquid ammonia, the metal combines with ozone.¹⁹ Some of its salts are poisonous.

Rubidium Ion — The univalent metal yields univalent ions, analogous to those of potassium, but has a greater electroaffinity, its salts being more readily ionized. This property manifests itself in the large heat of ionization,²⁰ 62.6 Cal., in the ready solubility of most of its salts, and in the comparatively slight tendency to form complex molecules.²¹ Only salts with strong anions, such as ClO₃', ClO₄', NO₃', Al(SO₄)₂, and PtCl₆', exhibit slight solubility.

Atomic Weight — Like the other alkali metals, rubidium is univalent, forming compounds of the type RbX, so that its hydrogen equivalent

¹ Guntz and Broniewski, *J. Chim. phys.*, 1909, 7, 464.

² Eckardt, *Ann. Physik*, 1900, 1, 790.

³ Guertler and Pirani, *Zeitsch. Metallkunde*, 1919, 11, 1.

⁴ Bunsen and Kirchhoff, *Pogg. Annalen*, 1861, 113, 373; Erdmann and Kothner, *Annalen*, 1897, 294, 56.

⁵ Rengade, *Compt. rend.*, 1913, 156, 1897; *Bull. Soc. chim.*, 1914 [4], 15, 130.

⁶ Ruff and Johannsen, *Ber.*, 1905, 38, 3601.

⁷ Dunoyer, *Le Radium*, 1912, 9, 218.

⁸ Bunsen and Kirchhoff, *loc. cit.*

⁹ Hackspill, *Compt. rend.*, 1911, 152, 259.

¹⁰ Erdmann and Kothner, *loc. cit.*

¹¹ Richards and Brink, *J. Amer. Chem. Soc.*, 1907, 29, 117.

¹² Sutton, *Trans. Chem. Soc.*, 1897, 71, 846; *Zeitsch. Kryst. Min.*, 1898, 29, 124; Sachs, *ibid.*, 1903, 38, 496; Marshall, *J. Amer. Chem. Soc.*, 1900, 22, 48.

¹³ Rengade, *Bull. Soc. chim.*, 1914 [4], 15, 130.

¹⁴ Hahn and Rothenbach, *Physikal. Zeitsch.*, 1919, 20, 194.

¹⁵ Campbell, *Proc. Camb. Phil. Soc.*, 1909, 15, 11.

¹⁶ Strong, *Amer. Chem. J.*, 1909, 42, 147.

¹⁷ Buchner, *Proc. K. Akad. Wetensch. Amsterdam*, 1909, 18, 91; compare Elster and GerTEL, *Physikal. Zeitsch.*, 1910, 11, 275; Henriot, *Le Radium*, 1910, 7, 40; *Compt. rend.*, 1911, 152, 851.

¹⁸ Hackspill and Bossuet, *Compt. rend.*, 1911, 152, 874.

¹⁹ Compare sodium, p. 86.

²⁰ Ostwald, *Grundriss der allgem. Chem.*, 3rd ed., Leipzig, 1899, 281.

²¹ Compare Abegg and Bodlander, *Zeitsch. anorg. Chem.*, 1899, 20, 462; Erdmann, *Arch. Pharm.*, 1894, 232, 25.

much more permeable to some gases than to others Other liquids have not been sufficiently examined in this respect

The mutual action of water, and the greater number of acid gases and alkaline gas partaking most evidently of a chemical nature, will be best considered under the heads of the respective acids and alkalis

SECTION 4

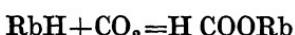
ON THE

CONSTITUTION OF SOLIDS

A solid body is one, the particles of which are in a state of equilibrium betwixt two great powers, attraction and repulsion, but in such a manner, that no change can be made in their distances without considerable force If an approximation of the particles is attempted by force, then the heat resists it, if a separation, then the attraction resists it The notion of Boscovich of alternating planes of attraction and repulsion seems unnecessary, except that upon forcibly breaking the cohesion of any body, the newly exposed surface must receive such a modification in its atmo-

atmosphere of hydrogen at 650° C for five days¹ It is a white, crystalline substance,² with density about 2 The vapour-tension for each temperature-interval of 10° between 350° and 450° C corresponds with the values 100, 114, 130, 160 200, 253, 322, 424, and 567 mm respectively A possible source of error may be the presence of carbon dioxide as the result of decomposition of the magnesium carbonate formed , but soda-lime was employed to absorb any carbon dioxide liberated, and the measurements were made rapidly¹ The tension increases rapidly to 85 mm at 230° C , and then slowly to 100 mm at 370° C

This hydride is more stable than that of caesium, but less stable than that of sodium or of potassium² It is very reactive When heated in vacuum at 300° C it decomposes into its constituent elements At ordinary temperatures it is attacked by the halogens Carbon dioxide converts it into rubidium formate



Under reduced pressure sulphur dioxide converts it into rubidium hyposulphite, $\text{Rb}_2\text{S}_2\text{O}_4$

Rubidium fluoride, RbF —The fluoride is obtained in anhydrous crystals by concentrating a solution of sodium carbonate neutralized with hydrofluoric acid³ Its melting-point is given as 753° C⁴ and 775° C⁵ The boiling-point is 1410° C , and the vapour-pressure in atmospheres is given by the expression⁶

$$\log p = -40000/4 57T + 5 243$$

It is very soluble in water, its heat of solution⁷ being 5 80 Cal Two hydrates are known,⁸ $2\text{RbF}, 3\text{H}_2\text{O}$, which melts at 36° C , and $\text{RbF}, 3\text{H}_2\text{O}$ They are very hygroscopic With hydrogen fluoride the fluoride yields the primary salt RbF, HF Other acid fluorides, $\text{RbF}, 2\text{HF}$, and $\text{RbF}, 3\text{HF}$, have also been prepared

Rubidium chloride, RbCl —The chloride is produced by the interaction of hydrochloric acid and rubidium carbonate, and also by heating rubidium chloroplatinate It forms lustrous cubes, stated to melt at 710° C⁹ 712° to 713° C¹⁰ 713° C¹¹ 714° C¹² 717° C¹³ and 726° C¹⁴ and to boil at 1383° C¹⁵ The vapour-pressure in atmospheres is given by the expression¹⁵

$$\log p = -37800/4 57T + 4 998$$

¹ Fphraim and Michel *Helv Chim Acta* 1921, 4 762

² Elster and Geitel *Physikal Zeitsch* 1910 11 257

³ Fggeling and Julius Meyer *Zeitsch anorg Chem* 1905 46 174

⁴ Carnelley *Trans Chem Soc* 1898 33 273

⁵ W. Wartenberg and Schulz *Zeitsch Elektrochem* 1921 27 568 compare Albrecht and Wartenberg *ibid* 162

W. Wartenberg and Schulz *loc cit*

⁷ de Forcand *Compt rend* 1911 152, 27

⁸ de Forcand, *ibid* 1208

⁹ Carnelley *loc cit*

¹⁰ Huttner and Tammann *Zeitsch anorg Chem* 1905 43 215

¹¹ Haigh *J Amer Chem Soc* 1912 34 1137

¹² Richards and Meldrum *ibid* 1917 39 1816

¹³ Wartenberg and Schulz *Zeitsch Elektrochem* 1921 27 568 compare Albrecht and Wartenberg *ibid* 162

¹⁴ Schemtschuschny and Rambach, *J Russ Phys Chem Soc*, 1909 41 1785

¹⁵ Wartenberg and Schulz, *loc cit*

Lead	$29\frac{1}{4}$	Pounds.
Tin	$49\frac{1}{4}$	
Copper.....	$299\frac{1}{4}$	
Brass.....	360	
Sil er...	370	
Iron	450	
Gold.....	.	500	

A piece of good oak, an inch square and a yard long, will just bear in the middle 330lbs But such a piece of wood should not in practice be trusted, for any length of time, with above $\frac{1}{3}$ or $\frac{1}{4}$ of that weight Iron is about 10 times as strong as oak, of the same dimensions

One would be apt to suppose that *strength* and *hardness* ought to be found proportionate to each other, but this is not the case Glass is harder than iron, yet the latter is much the stronger of the two

Crystallization exhibits to us the effects of the natural arrangement of the ultimate particles of various compound bodies, but we are scarcely yet sufficiently acquainted with chemical syntheses and analysis to understand the rationale of this process The rhomboidal form may arise from the proper position of 4, 6, 8 or 9 globular particles, the cubic form from 8 particles, the triangular form from 3,

cubes, its melting-point being given as $641.5^{\circ}\text{C}.$ ¹ and $642^{\circ}\text{C}.$ ² The boiling-point is $1305^{\circ}\text{C}.$ ³ and the vapour-pressure in atmospheres is given by the expression³

$$\log p = -37000/4.57T + 5.148$$

Its density is stated to be 3.028,⁴ 3.447,⁵ 3.428⁶ at $24.8^{\circ}\text{C}.$, and 3.438⁷ at $25^{\circ}\text{C}.$ At 17.4°C its solubility is 152 grams in 100 grams of water,⁸ the heat of solution being $-6.5\text{ Cal}.$ ⁹ Polyiodides such as $\text{RbI}_3,$ ¹⁰ $\text{RbI}_7,$ and RbI_9 ¹¹ have been isolated.

Rubidium chlorate, RbClO_3 —The chlorate is obtained by the interaction of rubidium sulphate and barium chlorate. On heating, it decomposes like potassium chlorate. It is less soluble in water than the corresponding potassium salt, the solubility at 19°C being 5.1 grams in 100 grams of water.¹²

Rubidium perchlorate, RbClO_4 —When rubidium chlorate is heated to a moderate temperature, it is converted into a mixture of perchlorate and chloride. The perchlorate is isomorphous with the corresponding potassium salt, but is less soluble in water, the solubility at 21.8°C being 1.09 grams in 100 grams of water.¹³

Rubidium iodate, RbIO_3 —Iodic anhydride reacts with rubidium carbonate to form the iodate, and the salt is also produced by passing chlorine into a hot concentrated solution of rubidium iodide and hydroxide.¹⁴ It forms monoclinic crystals isomorphous with those of potassium iodate, and of density 4.559 at $14^{\circ}\text{C}.$ At 23°C the solubility is 2.1 grams in 100 grams of water.¹⁵ It yields acid iodates,¹⁵ such as $\text{RbIO}_3 \cdot \text{HIO}_3$ and $\text{RbIO}_3 \cdot 2\text{HIO}_3$, and also compounds of the type $\text{RbIO}_3 \cdot \text{F}_2$ ¹⁶ and $\text{RbIO}_3 \cdot \text{HIO}_3 \cdot 4\text{HF}$.¹⁷

Rubidium periodate, RbIO_4 —When a mixture of rubidium iodate and hydroxide in hot concentrated solution is oxidized with chlorine, the periodate is formed in colourless quadratic crystals isomorphous with those of potassium periodate, and with the density 3.918 at $16^{\circ}\text{C}.$ At 18°C its solubility is 0.65 gram in 100 grams of water.¹⁸

Rubidium monoxide, Rb_2O —When rubidium is partially oxidized by diluted oxygen, and the excess of metal removed by distillation, the

¹ Victor Meyer Riddle, and Lamb *Ber* 1893 **26** 3129

² Carnelley *Trans Chem Soc*, 1898 **33**, 273

³ Wartenberg and Schulz *Zeitsch Elektrochem* 1921 **27**, 568, compare Albrecht and Wartenberg *ibid* 162

⁴ Compare Schroder *Annalen*, 1878 **192**, 295

⁵ Lrdmann *Arch Pharm* 1894 **232** 25

⁶ Buchanan *Proc Chem Soc* 1905 **21**, 122

⁷ Baxter and Brink *J Amer Chem Soc* 1908 **30** 46

⁸ Reissig *Annalen* 1863 **127** 34

⁹ de Forcand *Compt rend* 1911 **152** 27

¹⁰ Wells and Wheeler *Zeitsch anorg Chem* 1892 **1**, 442 **2**, 257, compare Foote and Chalker *Amer Chem J* 1908 **39** 561

¹¹ Abegg and Hamburger *Zeitsch anorg Chem*, 1906 **50**, 403

¹² Reissig *loc cit*

¹³ Louguimine *Annalen*, 1862 **121** 123

¹⁴ Barker *Trans Chem Soc* 1908 **93** 15

¹⁵ Wheeler *Amer J Sci* 1902 [3] **44** 123

¹⁶ Weinland and Lauenstein *Zeitsch anorg Chem* 1899 **20**, 30 Weinland and Alfa *ibid* 1899 **21** 53

¹⁷ Weinland and Koppen *ibid* 1900, **22** 260 Weinland and Bartlingck *Be* 1903 **36**, 1401

¹⁸ Barker *loc cit*

its dignity by keeping all the rest, which by their gravity, or otherwise are disposed to encroach upon it, at a respectful distance When we attempt to conceive the *number* of particles in an atmosphere, it is somewhat like attempting to conceive the number of stars in the universe, we are confounded with the thought But if we limit the subject, by taking a given volume of any gas, we seem persuaded that, let the divisions be ever so minute, the number of particles must be finite, just as in a given space of the universe, the number of stars and planets cannot be infinite

Chemical analysis and synthesis go no farther than to the separation of particles one from another, and to their reunion No new creation or destruction of matter is within the reach of chemical agency We might as well attempt to introduce a new planet into the solar system, or to annihilate one already in existence, as to create or destroy a particle of hydrogen All the changes we can produce, consist in separating particles that are in a state of cohesion or combination, and joining those that were previously at a distance

In all chemical investigations, it has justly been considered an important object to ascertain the relative *weights* of the simples which

microscopic white needles belonging to the cubic system, and isomorphous with those of the corresponding salt of potassium, but not with those of caesium monosulphide. Its density is 2.912, and it melts at the temperature of softening of glass. It dissolves in water with a hissing sound, the heat of solution being 24.6 Cal. The heat of formation of the solid from its elements is 87.1 Cal., and that from rubidium hydroxide and hydrogen sulphide is 8.0 Cal. Rubidium monosulphide is readily oxidized, is combustible, and weathers in air.¹

The monosulphide is converted by sulphur in an atmosphere of hydrogen into the pentasulphide, Rb_2S_5 , deliquescent, red crystals melting at 223° to 224° C, and of density 2.618 at 15° C. When heated in nitrogen it yields the trisulphide, Rb_2S_3 , consisting of hygroscopic, dark-yellow crystals melting at 213° C, but in hydrogen the hygroscopic disulphide, Rb_2S_2 , is formed, a substance melting about 420° C and boiling above 950° C. Both the disulphide and the trisulphide yield a monohydrate. The tetrasulphide, Rb_2S_4 , is formed by heating the monosulphide with the calculated amount of sulphur. It yields a yellow, crystalline dihydrate. *Rubidium hydrogen sulphide*, $RbSH$, is produced by saturating a solution of rubidium hydroxide with hydrogen sulphide.

Rubidium sulphate, Rb_2SO_4 .—The sulphate forms rhombic crystals isomorphous² with those of potassium sulphate, melting³ at 1074° C, the density at 20° C being 3.6118, and at 60° C 3.5948.⁴ It exists in two modifications,⁵ the transition point being 657° C. The heat of formation from the elements is 844.68 Cal., and the heat of solution —6.66 Cal at 15° C.⁶ The solubility⁷ is given in the appended table.

Solubility of Rubidium Sulphate

Temperature, °C	0	10	20	30	40	50	60	70	80	90	100
Grams of Rb_2SO_4 per 100 g of water	36.4	42.6	48.2	53.5	58.5	63.1	67.4	71.4	75.0	78.7	81.8

The boiling point of the saturated solution in contact with excess of sulphate is 103.5° C at 760 mm pressure.⁸ With aluminium and ferric sulphates it forms well crystallized alums. It exhibits radioactivity.⁹

Rubidium hydrogen sulphate, $RbHSO_4$.—The primary sulphate has a density at 16° C of 2.892.¹⁰ Its heat of formation from the elements is 277.37 Cal., and its heat of solution —3.73 Cal.¹¹ On ignition it is converted into *rubidium pyrosulphate*, $Rb_2S_2O_7$.

Rubidium persulphate, $Rb_2S_2O_8$.—The persulphate is formed by the

¹ Rengade and Costeanu *Compt rend* 1913 156, 791 1914 158, 946

² See p. 227

³ Huttner and Tammann *Zeitsch anorg Chem* 1905 43, 215

⁴ Tutton *Trans Chem Soc* 1894, 65, 628 1896 69, 344

⁵ Huttner and Tammann *loc cit*

⁶ de Forcrand *Compt rend* 1906 143, 98

⁷ Landolt Bornstein and Meyerhoffer *Tabellen* 3rd ed Berlin 1905 566 compare Earl of Berkeley *Phil Trans* 1904 [A], 203, 207 Étard *Ann Chim Phys* 1894 [7] 2, 550

⁸ Earl of Berkeley and Applebey *Proc Roy Soc* 1911 [A] 85, 489

⁹ Buchner *Le Radium* 1912 9, 259

¹⁰ Spring *Bull Acad roy Belg* 1904 290

¹¹ de Forcrand *loc cit*

The following general rules may be adopted as guides in all our investigations respecting chemical synthesis

1st When only one combination of two bodies can be obtained, it must be presumed to be a *binary* one, unless some cause appear to the contrary

2d When two combinations are observed, they must be presumed to be a *binary* and a *ternary*

3d When three combinations are obtained, we may expect one to be a *binary*, and the other two *ternary*

4th When four combinations are observed, we should expect one *binary*, two *ternary*, and one *quaternary*, &c

5th A *binary* compound should always be specifically heavier than the mere mixture of its two ingredients

6th A *ternary* compound should be specifically heavier than the mixture of a *binary* and a simple, which would, if combined, constitute it, &c

7th The above rules and observations equally apply, when two bodies, such as C and D, D and E, &c are combined

From the application of these rules, to the chemical facts already well ascertained, we

interaction of rubidium sulphate and barium hydrazoate.¹ It forms tetragonal plates melting at 330° to 340° C, which display marked double refraction. It is not very explosive, but melts between 330° and 340° C with evolution of gas. The solubility at 16° C is 107.1 grams in 100 grams of water, the solution having a slightly alkaline reaction.

Rubidium nitrite, RbNO₂.—Barium nitrite and rubidium sulphate interact to form rubidium nitrite, a yellowish, crystalline substance, very soluble in water.²

Rubidium nitrate, RbNO₃.—The nitrate is trimorphous,³ crystallizing in hexagonal,⁴ cubic, and bi-refractive forms, the transition-points in the order named being 161.4° C and 218.9° to 219.3° C. The crystals are very hard, melt at 318° C,⁵ and have a density of 3.131⁶ at 15° C and 3.112 at 20° C.⁷ The molecular electric conductivity of rubidium nitrate between 318.8° and 498° C is given by the formula⁸

$$\mu_t = 33.51 + 0.145(t - 300)$$

The solubility in water⁹ is given in the table

Solubility of Rubidium Nitrate

Temperature, °C	0	10	20	30	40	50	60	70	80	90	100
Grams of RbNO ₃ per 100 g of water	19.5	33.0	53.3	81.3	116.7	155.6	200	251	309	375	452

A saturated solution containing 61.7 grams in 100 grams of water boils at 118.3° C under a pressure of 734 mm of mercury. In chemical properties the salt resembles potassium nitrate. It exhibits radioactivity.¹⁰ With nitric acid it yields acid nitrates,¹¹ RbNO₃.HNO₃, melting at 62° C, and RbNO₃.2HNO₃, melting at 39° to 46° C.

Rubidium phosphide, Rb₂P₅.—The phosphide is formed by the interaction of phosphorus and rubidium hydride, and also by Hackspill and Bossuet's method (p. 136). In properties it resembles closely the corresponding potassium derivative, and has a density of 2.5.¹²

Rubidium phosphates.—The three phosphates are prepared by the interaction of phosphoric acid and rubidium hydroxide or carbonate in appropriate proportions.¹³ The primary phosphate, RbH₂PO₄, is acidic in aqueous solution, the other two are alkaline. When heated at 244° C the primary phosphate loses water, yielding the acid pyro phosphate, Rb₂H₂P₂O₇.¹⁴ The secondary phosphate forms a monohydrate,

¹ Curtius and Rissom *J. prakt. Chem.*, 1898 [2] 58, 280 compare Dennis and Benedikt, *Zeitsch. anorg. Chem.* 1898 17 20

Ball and Abram *Trans. Chem. Soc.* 1914 103 2130

² Schwarz *Landolt-Bornstein and Meyerhoffer's Tabellen* 3rd ed. Berlin 1905 283

³ Compare Jaeger *Zeitsch. Kryst. Min.* 1907 43 588 Duffour *Bull. Soc. franç. Min.* 1913 36 136

Haigh *J. Amer. Chem. Soc.* 1912, 34, 1137

⁴ Retgers *Zeitsch. physikal. Chem.* 1889 4 597

⁵ Haigh *loc. cit.*

⁶ Jaeger and Kapma *Zeitsch. anorg. Chem.* 1920, 113 27

⁷ Earl of Berkeley *Phil. Trans.* 1904 [A] 203 207 compare Landolt-Bornstein and Meyerhoffer *Tabellen* 3rd ed., Berlin, 1905 566

¹⁰ Buchner *Le Radium* 1912 9 259

¹¹ Wells and Metzger, *Amer. Chem. J.*, 1901, 26, 271

¹² Compare Bossuet and Hackspill *Compt. rend.*, 1913, 157, 720

¹³ Von Berg *Ber.*, 1901 34, 4181

¹⁴ Balareff, *Zeitsch. anorg. Chem.*, 1921, 118, 123

In the sequel, the facts and experiments from which these conclusions are derived, will be detailed, as well as a great variety of others from which are inferred the constitution and weight of the ultimate particles of the principal acids, the alkalis, the earths, the metals, the metallic oxides and sulphurets, the long train of neutral salts, and in short, all the chemical compounds which have hitherto obtained a tolerably good analysis. Several of the conclusions will be supported by original experiments.

From the novelty as well as importance of the ideas suggested in this chapter, it is deemed expedient to give plates, exhibiting the mode of combination in some of the more simple cases. A specimen of these accompanies this first part. The elements or atoms of such bodies as are conceived at present to be simple, are denoted by a small circle, with some distinctive mark, and the combinations consist in the juxtaposition of two or more of these, when three or more particles of elastic fluids are combined together in one, it is to be supposed that the particles of the same kind repel each other, and therefore take their stations accordingly.

or higher. Its properties are similar to those of the corresponding potassium salt¹

DETECTION AND ESTIMATION OF RUBIDIUM

Rubidium salts impart a reddish-violet coloration to the Bunsen flame, similar to that characteristic of potassium derivatives. Like potassium, rubidium forms several salts not readily soluble, among them the chloroplatinate, perchlorate, silicofluoride, bismuth thiosulphate, and primary tartrate. It can also be detected by the formation of $\text{Bi}(\text{NO}_3)_3 \cdot 2\text{RbNO}_2 \cdot \text{NaNO}_2$, a yellow crystalline precipitate produced by adding a solution of bismuth nitrate and sodium nitrite to one of a rubidium salt²

Rubidium chloride yields a complex rubidium-silver-gold chloride, separating in blood-red prisms. The formation of this precipitate is an aid in the microchemical identification of rubidium, and serves to detect one tenth of a microgram of the element³

The metal can be estimated as chloride or sulphate, or by heating the sulphate with sulphuric acid and the sulphate of an alkaline-earth metal such as calcium, a double sulphate of the type $\text{Rb}_2\text{SO}_4 \cdot \text{CaSO}_4$ being formed and weighed⁴

¹ Rosenheim and Leyser, *Zeitsch anorg Chem*, 1921, 119, 1

² Ball, *Trans Chem Soc*, 1909, 95, 2126

³ Bayer, *Monatsh*, 1920, 41, 223, compare Emich, *ibid*, 243

Mackenzie and Marshall, *Trans Chem Soc*, 1908, 93, 1726. On the separation from sodium and potassium, compare Vernadski, *Bull Soc franç Min*, 1913, 36, 258

2

N.W.
Old
Scale7000
6000
50004000
30002000
1000500
200B
200100
0100
0100
0100
0

Vapour

Water

Ice

7000

212°
32°

3000

2000

1000

500

200

100

100
0

200

190

180

170

160

150

140

130

120

110
100
90
80
70
60
50
40

at 26° C, 1886 at 27° C, and 1827¹ at 40° C. The atomic volume is 71, and is higher than that of any other element.² At absolute zero the density is 2222, and the corresponding atomic volume is 5977³. The specific heat is 0.04817 between 0° and 26° C,⁴ and is given by Rengade⁵ as 0.0600 at 0° C. The heat of fusion of 1 gram is given as 3.78 cal, and also⁵ as 3.76 cal. It is the softest metal, the hardness on Rydberg's⁶ scale being 0.2. Neither the metal nor any of its salts displays radioactivity.⁷

Chemical Properties—In chemical properties cæsium is closely related to potassium and rubidium. When brought into contact with air, it undergoes rapid oxidation, and the pure metal ignites in dry oxygen at the ordinary temperature.⁸ It decomposes water energetically, the action on ice beginning at -116° C.⁹ Its solution in liquid ammonia reacts with ozone.¹⁰

Cæsium Ion—Cæsium forms colourless univalent ions. It is the most electropositive of the elements, its great electroaffinity corresponding with the ready solubility of its salts. The salts with strong anions are less soluble than the corresponding derivatives of the other alkali-metals.¹¹

Atomic Weight—The chemical properties of cæsium indicate its close relationship to the other alkali-metals. It is univalent, forming compounds of the type CsX, its atomic weight and hydrogen equivalent being the same. Its atomic weight is of the order Cs=133, a value confirmed by the specific-heat method (Vol. I, p. 88), by the isomorphism of the cæsium compounds with those of potassium, ammonium, and rubidium (Vol. I, p. 74), by the correspondence of the properties of the metal and its compounds with the periodic system, by the formation of a univalent cation, and by the depression of the freezing-point of bismuth chloride and mercuric chloride produced by cæsium chloride.

Early Determinations

The earliest determination of the atomic weight of cæsium with any approach to accuracy was that of Johnson and Allen.¹² The mean of four experiments gave the value

$$\text{AgCl} \text{ CsCl} = 100 \text{ } 117\ 499,$$

¹ Fockhardt und Grafe *Zeitsch. anorg. Chem.* 1900 **23** 378

² Compare Rudorf *Das Periodische System* Hamburg 1904 129

³ Herz *Zeitsch. anorg. Chem.* 1921 **120**, 159 compare Herz *ibid.* 1919 **105** 171, Lorenz und Herz *ibid.* 1921 **117** 267

⁴ Fockhardt und Grafe *loc. cit.*

⁵ Rengade *Bull. Soc. chim.* 1914 [4] 15, 130

⁶ Rydberg *Zeitsch. physikal. Chem.* 1900 **33** 353

⁷ Compare Levin and Ruhr *Physikal. Zeitsch.* 1909 **10** 576 Elster and Geitel *ibid.* 1910 **11** 275 Henriot *Le Radium* 1910 **7** 40 *Compt. rend.*, 1911 **152** 851 Buchner *Le Radium* 1912 **9** 259, compare Hahn and Rothenbach *Physikal. Zeitsch.*, 1919 **20** 194

⁸ Rengade *Compt. rend.* 1906 **142** 1533 1907, **145**, 236 *Ann. Chim. Phys.*, 1907 [8] **11** 348

⁹ Hackspill and Bossuet *Compt. rend.* 1911, **152** 874

¹⁰ Compare the section on sodium p. 86

¹¹ Compare Abegg and Bodlander *Zeitsch. anorg. Chem.* 1899 **20** 462

¹² Johnson and Allen *Amer. J. Sci.*, 1863 [2] 35 94

curve, represent equal intervals of temperature (25° steam or aqueous vapour, and 34° for ethereal vapour) the ordinates represent inches of mercury, the weight which is equal to the force of steam at the temperature. See the 8th and 9th columns of table, at page 14. Thus force of steam at 212° , and of ethereal vapour at 11° new scale, is equal to 30 inches of mercury, at 187° force of steam is half as much, or 15 inches, and at 7° that of ethereal vapour is also 15 inches, &c.

Fig 3 is a device suggested by Mr Ewart, to illustrate the idea which I have developed in the section on the temperature of the atmosphere. It is a cylindrical vessel closed at one end and open at the other, having a moveable piston sliding within it. The vessel is supposed to contain air and a weight is connected with the piston as a counterpoise to it. There is also a thermometer supposed to pass through the side of the vessel, and to be cemented into it. Now if we may suppose the piston to move with friction, and the vessel to be taken up into the atmosphere, the piston will gradually ascend, and suffer the air within to dilate, so as to correspond every where with the external air in density. This dilatation tends to diminish the temperature of the air within (provided no heat is acquired from the vessel). Such an instrument would shew what the theory requires, namely, that the temperature of air within would every where in the same vertical column agree with that without, though the former would not receive or part with any heat absolutely, or in any manner communicate with the external air.

PLATE III See page 135 — The balls in Fig 1 and 2 represent particles of water in the former the square form denotes the arrangement in water, the rhombo form in the latter, denotes the arrangement in ice. The angle is always 60° or 120° .

Fig 3 represents the perpendicular section of a triangle resting upon two others, as 4 and 5, Fig 1.

Fig 4 represents the perpendicular section of a triangle resting upon two balls, as 7 and 5, Fig 2. The perpendiculars of the triangles shew the heights of the strata in the two arrangements.

Fig 5 represents one of the small spiculae of ice formed upon the sudden congelation of water cooled below freezing point. See page 134.

Fig 6 represents the shoots or ramifications of ice during the commencement of congelation. The angles are 60° and 120° .

COMPOUNDS OF CÆSIUM.¹

Cæsium hydrde, CsH — It is difficult to prepare the hydrde in a state of purity. It can be obtained in the form of white crystals by the interaction of pure cæsium and pure hydrogen, its general characteristics being similar to those of the corresponding rubidium derivative.² Ephraim and Michel³ produced it by heating a mixture of cæsium carbonate and metallic magnesium in hydrogen at 580° to 620° C for three days. It is the least stable of the alkali-metal hydrides. Its density⁴ is 2.7. Ephraim and Michel³ found the vapour tension for each interval of 10° between 340° and 440° C to be 78, 100, 126, 160, 202, 256, 317, 402, 508, 630, and 787 mm., but the measurements may have been vitiated by the presence of carbon dioxide arising from decomposition of the magnesium carbonate formed, by the sublimation of the metal, and by its solubility in the hydrde.

Cæsium fluorides — Evaporation of a solution of cæsium carbonate in hydrofluoric acid yields the *primary fluoride*, CsF, HF.⁵ When heated, this substance is converted into the *normal fluoride*, CsF, which crystallizes in cubes, melts at 684° C,⁶ and boils at 1251° C.⁶ Its vapour-pressure in atmospheres corresponds with the expression⁶

$$\log p = -84700/4\ 57T + 4\ 982$$

The anhydrous fluoride yields two very deliquescent hydrates, CsF, 1 5H₂O, and 3CsF, 2H₂O.⁷ The heat of solution of the anhydrous salt is 8.37 Cal.⁸

Cæsium chloride, CsCl — The chloride is prepared similarly to that of rubidium. It forms cubes, melting at 626° C,⁹ 631° C,¹⁰ 645° C,¹¹ 646° C¹² or 647° C,¹³ and boiling at 1303° C.¹⁴ The vapour pressure in atmospheres is given by the expression¹⁴

$$\log p = -37400/4\ 57T + 5\ 190$$

The substance has a density of 3.972¹⁵ or 3.987¹⁶ at 20° C, and 3.982¹⁷ at 23.1° C. Its latent heat of fusion per gram is 0.024 Cal.¹⁸ The

¹ Attention is called to the close analogy in modes of preparation and properties of the cæsium and rubidium compounds. For *cæsium amalgam*, see this series Vol III Moissan *Compt rend.*, 1903, 136, 587 1177, Elster and Geitel *Physikal Zeitsch* 1910 II 257

² Ephraim and Michel *Helv Chim Acta*, 1921, 4, 762

³ Moissan *loc cit*

⁴ Chabrié *Compt rend.* 1901 132 680

⁵ Wartenberg and Schulz *Zeitsch Elektrochem.*, 1921, 27, 568 compare Albrecht and Wartenberg *ibid* 162

⁶ de Forcrand *Compt rend.* 1911, 152 1208

⁷ de Forcrand, *ibid.*, 27

⁸ Wartenberg and Schulz, *Zeitsch Elektrochem.* 1921, 27, 568 compare Albrecht and Wartenberg *ibid* 162

¹⁰ Caincley and Williams *Trans Chem Soc* 1880 37 125

¹¹ Richards and Meldrum *J Amer Chem Soc* 1917, 39 1816

¹ Schemtschuschny and Rambach *J Russ Phys Chem Soc* 1909, 41 1785

¹³ Haigh *J Amer Chem Soc* 1912, 34 1137

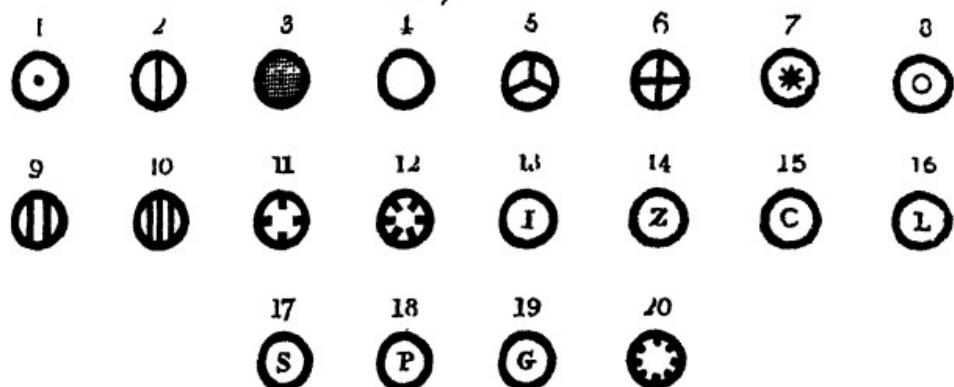
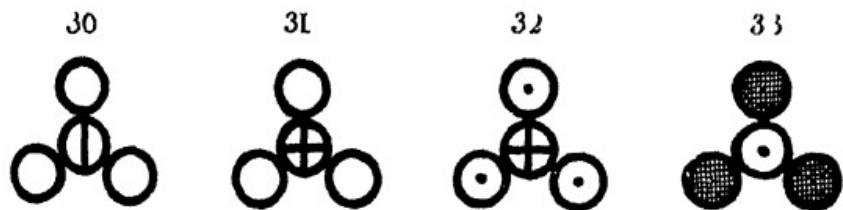
¹⁴ Wartenberg and Schulz *loc cit*

¹⁵ Richards and Archibald, *Zeitsch anorg Chem.*, 1903, 34, 353

¹⁶ Haigh, *loc cit*

¹⁷ Buchanan, *Proc Chem Soc*, 1905 21, 122

¹⁸ Schemtschuschny and Rambach, *loc cit*

Simple*Binary**Ternary**Quaternary**Quintenary & Sextenary*

34 35

*Septenary*

36 37



solution is -8.25 Cal¹. A *tri-iodide* and a *pentaiodide* have been isolated,² and the existence of a *heptaiodide* and of an *enneaiodide*, CsI_9 , is probable.³

Cæsium chlorate, CsClO_3 .—The chlorate has been little investigated.⁴

Cæsium bromate, CsBrO_3 .—The preparation of cæsium bromate has been effected by McCrosky and Buell,⁵ and is stated to be carried out best in acid solution. It crystallizes without water of crystallization, and melts at a higher temperature than potassium bromate. At 30° C 100 grams of water dissolve 4.53 grams of the salt.

Cæsium iodate, CsIO_3 .—The iodate is precipitated by the action of chlorine on a hot concentrated solution of cæsium iodide and hydroxide.⁶ It yields monoclinic crystals, isomorphous with the corresponding salts of rubidium and potassium, and of density 4.881 at 16° C . At 24° C its solubility is 2.6 grams in 100 grams of water.⁷

Cæsium periodate, CsIO_4 .—The periodate is prepared by the action of cæsium carbonate on periodic acid.⁸ It forms orthorhombic plates, not isomorphous with the corresponding salts of rubidium and potassium.⁹ It has a density of 4.259 at 15° C , and its solubility at 15° C is 2.15 grams in 100 grams of water.

Cæsium monoxide, Cs_2O .—The monoxide is prepared by incomplete oxidation of the metal at ordinary temperature, the excess being removed by vacuum-distillation at 180° to 200° C .¹⁰ It forms scarlet-red crystals,¹¹ which become purple-red at a temperature above the ordinary, and black at 150° C . At -180° C their colour is bright yellow. The substance melts at 450° to 500° C , decomposing into the metal and the peroxide, Cs_2O_2 . At 0° C it has a density of 4.36,¹² (water at $0^\circ\text{ C} = 1$). Its heat of formation is 82.7 Cal,¹³ and its heat of solution is 88.2 Cal.¹⁴ From the air it absorbs moisture and carbon dioxide, becoming white and deliquescent. It dissolves to a clear solution in water, the process being attended by a hissing sound and the production of flame. In moist carbon dioxide it ignites at the ordinary temperature. Hydrogen reduces it to the hydride and hydroxide.

Cæsium suboxides.—Two suboxides have been isolated,¹⁵ Cs_7O , a bronze coloured solid, melting at 3° C , and Cs_7O_2 , long prisms of permanganate colour. Both are formed by fusion of the monoxide with cæsium, the fusion curve indicating the existence of two other suboxides, Cs_4O and Cs_3O .

Cæsium peroxides.—Three peroxides have been prepared by heating

¹ de Forcand *Compt rend*, 1911, 152, 27.

² Wells and Wheeler *Zeitsch anorg Chem* 1892 1, 442, 2 237.

³ Abegg and Hamburger *ibid* 1906 50 403 compare loote *Amer Chem J* 1903

²⁹ 203 Dawson and Goodson *Trans Chem Soc* 1904 85 796

⁴ Compare Baur *Zeitsch physikal Chem* 1895 18 184.

⁵ McCrosky and Buell *J Amer Chem Soc*, 1920 42 1786.

⁶ Barker *Trans Chem Soc* 1908 93 15.

⁷ Wheeler *Amer J Sci* 1902, [3] 44, 123.

⁸ Wells *Amer Chem J* 1901, 26 278.

⁹ Barker *loc cit*

¹⁰ Rengade *Compt rend* 1906, 143 592 1907 144 753.

¹¹ Rengade, *ibid* 1909 148 1199 *Bull Soc chim* 1909 [4] 5 994.

¹² Rengade, *Bull Soc chim* 1907 [4] 1 666.

¹³ Rengade, *Compt rend* 1908 146 129 de Forcand *ibid* 1914 158 991.

¹⁴ Rengade, *ibid*, 1908 146, 129.

¹⁵ Rengade, *ibid* 1909 148, 1199 *Bull Soc chim* 1909 [4] 5 994.

Enough has been given to shew the method, it will be quite unnecessary to devise characters and combinations of them to exhibit to view in this way all the subjects that come under investigation, nor is it necessary to insist upon the accuracy of all these compounds, both in number and weight, the principle will be entered into more particularly hereafter, as far as respects the individual results. It is not to be understood that all those articles marked as simple substances, are necessarily such by the theory, they are only necessarily of such weights. Soda and Potash, such as they are found in combination with acids, are 28 and 42 respectively in weight, but according to Mr Davy's very important discoveries, they are metallic oxides, the former then must be considered as composed of an atom of metal, 21, and one of oxygen, 7, and the latter, of an atom of metal, 35, and one of oxygen, 7. Or, soda contains 75 per cent metal and 25 oxygen, potash, 83 3 metal and 16 7 oxygen. It is particularly remarkable, that according to the above-mentioned gentleman's essay on the Decomposition and Composition of the fixed alkalies, in the Philosophical Transactions (a copy of which essay he has just favoured me with) it appears that "the largest quantity of oxygen indicated by these experiments was, for potash 17, and for soda, 26 parts in 100, and the smallest 13 and 19."

DIRECTIONS TO THE BINDER

- Plate 1 to face page 217
- 2 to face page 218
- 3 to follow plate 2
- 4 to face page 219

yield a monohydrate. The *tetrasulphide*, Cs_2S_4 , is anhydrous. The *pentasulphide*, Cs_2S_5 , melts at 204° to 205° C, and its density at 16° C is 2.806.

Cæsium sulphites¹—The *normal sulphite*, Cs_2SO_3 , is prepared by addition of an equivalent proportion of cæsium carbonate to an alcoholic solution of the salt saturated with sulphur dioxide. It forms white, readily soluble crystals.

The *primary sulphite*, CsHSO_3 , is prepared by the action of sulphur dioxide on an alcoholic solution of the carbonate. It is a white, crystalline salt, very soluble in water.

Cæsium sulphate, Cs_2SO_4 —The sulphate is produced by the interaction of cæsium chloride and sulphuric acid². It forms rhombic crystals,³ melting at 995° C⁴ or 1019° C⁵. Its density at 16° C is 4.260⁶, at 20° C, 4.2433, and at 60° C, 4.2218⁷.

The solubility⁸ is given in the table.

Solubility of Cæsium Sulphate

Temperature, °C	0	10	20	30	40	50	60	70	80	90	100
Grams of Cs_2SO_4 per 100 grams of water	167.1	173.1	178.7	184.1	189.4	194.9	199.9	205.0	210.3	214.9	220.3

A saturated solution boils at 110° C at 760 mm pressure⁹. The salt is almost insoluble in alcohol. The heat of formation from the elements has been calculated¹⁰ to be 349.8 Cal. It forms well-crystallized double salts with the sulphates of lithium, ferric iron, aluminium, and bivalent metals.

Cæsium hydrogen sulphate, CsHSO_4 —The primary sulphate crystallizes in rhombic prisms,¹¹ of density 3.352¹² at 16° C. Its heat of formation from the elements is 282.9 Cal, and its heat of solution —3.73 Cal.¹³

Another *acid sulphate*, $\text{Cs}_2\text{O}_8\text{SO}_3$, and the *pyrosulphate*, $\text{Cs}_2\text{S}_2\text{O}_7$, have been prepared.¹⁴

Cæsium persulphate, $\text{Cs}_2\text{S}_2\text{O}_8$ —The persulphate is produced by electrolysis of a concentrated solution of the sulphate.¹⁵

Cæsium thiosulphate, $\text{Cs}_2\text{S}_2\text{O}_3$ —The thiosulphate is formed on addition of sulphur to a boiling solution of the sulphite,¹⁶ and also by the action of the carbonate on barium thiosulphate.¹⁷ It crystallizes in small, very soluble needles.

¹ Chabrie *Compt rend.*, 1901, 132, 680.

Foote *J Amer Chem Soc*, 1911, 33, 463.

² For isomorphism, see p. 227.

⁴ Muller *N Jährb Mineral Beil Bd* 1914, 30, 1. *Zeitsch Kryst Min* 1914, 53, 511.

⁵ Huttner and Tammann *Zeitsch anorg Chem*, 1905, 43, 215.

⁶ Spring *Bull Acad roy Belg* 1904, 290.

⁷ Tutton *Zeitsch Kryst Min* 1895, 24, 1.

⁸ Landolt Bornstein and Meyerhofer *Tabellen* 3rd ed Berlin 1905, 534. Earl of Berkeley *Phil Trans* 1904 [A], 203, 207.

⁹ Earl of Berkeley and Applebey *Proc Roy Soc* 1911 [A], 85, 489.

¹⁰ de Forcrand *Compt rend* 1906, 143, 98.

¹¹ Bunsen and Kirchhoff *Pogg Annalen* 1861, 113, 342; 1863, 119, 1. *Annalen* 1862, 347, 1863, 125, 367.

¹² Spring *loc cit*.

¹³ de Forcrand *loc cit*.

¹⁴ Weber *Ber* 1884, 17, 2500.

¹⁵ Foster and Smith *J Amer Chem Soc*, 1899, 21, 934.

¹⁶ Chabrié *Compt rend* 1901, 133, 295.

¹⁷ Julius Meyer and Eggeling, *Ber* 1907, 40, 1351.

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The molecular electric conductivity of cæsium nitrate between 446.6° and 556.3° C. is given by the formula¹

$$\mu_t = 42.13 + 0.120(t - 450)$$

A saturated solution in contact with excess of the salt boils at 107.2° C under 760 mm pressure². Its solubility in absolute alcohol is very slight. With nitric acid it yields *acid nitrates*³ of the type CsNO₃, HNO₃, m.p. 100° C., and CsNO₃, 2HNO₃, m.p. 32° to 36° C.

Cæsium phosphide, Cs₂P₅—The phosphide resembles the corresponding potassium derivative (p. 181). It can be prepared by Hackspill and Bossuet's method (p. 181, reference 3).

Cæsium phosphates—In constitution and properties the phosphates resemble the corresponding salts of rubidium. They are prepared by analogous methods⁴.

Cæsium carbide, Cs₂C₂—The carbide is prepared from cæsium acetylhyde, Cs₂C₂, C₂H₂, by a method similar to that employed for the corresponding rubidium compound⁵.

Cæsium carbonate, Cs₂CO₃—The normal carbonate is produced by the interaction of the hydroxide and ammonium carbonate⁶. It forms deliquescent, hydrated crystals, the anhydrous salt being very hygroscopic, and melting at red heat. When heated in vacuum it loses carbon dioxide. It is soluble in water to a very alkaline solution, the heat of solution being 11.84 Cal⁷. At 20° C the saturated solution contains 72.34 per cent of the anhydrous salt. Several hydrates are known. The heat of formation of the anhydrous salt is 274.54 Cal⁸.

Cæsium hydrogen carbonate, CsHCO₃—The primary carbonate is formed by the action of carbon dioxide on the normal carbonate,⁹ and crystallizes in long, anhydrous prisms, stable up to 125° C, but decomposing at 175° C with evolution of carbon dioxide and formation of the normal carbonate. At 20° C its solubility is higher than that of the corresponding potassium salt, being 67.77 grams in 100 grams of water; that of potassium hydrogen carbonate is 33.2 grams. At 15° C the heat of solution is -4.317 Cal. The heat of formation from the elements is 232.92 Cal. The dissociation pressure has been studied by Caven and Sand¹⁰. Other primary carbonates are formed by the action of atmospheric carbon dioxide on a solution of cæsium carbonate.

Cæsium percarbonate, Cs₂C₂O₆—A solution of the percarbonate has been obtained by the electrolysis of a solution of cæsium carbonate¹¹.

Cæsium metasilicate, Cs₂SiO₃—An investigation has been made of the properties of the metasilicate in dilute aqueous solution¹².

¹ Jaeger and Kapma *Zeitsch. anorg. Chem.* 1920 113, 27

Furl of Berkeley and Applebey *Proc. Roy. Soc.* 1911 [A] 85 489

³ Wells and Metzger *Amer. Chem. J.* 1901 26 271

⁴ Von Berg, *Ber.* 1901 34 4181

Moissnn *Compt. rend.* 1903 136 1221 1522

⁶ Bunsen and Kirchhoff *Pogg. Annalen* 1861, 113 342 1863 119 1 *Annalen* 1862 122 347 1863 125 367

⁷ de Forcrand *Compt. rend.* 1909 149 97

⁸ de Forcrand *ibid.* 719

⁹ de Forcrand *ibid.* 719 825 compare Bunsen and Kirchhoff *loc. cit.*

¹⁰ Caven and Sand *Trans. Chem. Soc.* 1914 105 2755

¹¹ Priesenfeld and Reinhold *Ber.* 1909 42 4377

¹² Kahlenberg and Lincoln *J. Physic. Chem.* 1898 2 82

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3

CHAPTER VIII

AMMONIUM COMPOUNDS

Occurrence—Small quantities of ammonium salts are widely distributed over the surface of the earth and throughout the ocean. They are present in the Stassfurt deposits. The sulphate and chloride have been found in the neighbourhood of active volcanoes, and the borate is present in the boric-acid softioni. A mineral called *struvite*, $MgNH_4PO_4$, is a product of the decomposition of animal excrement in the soil.

History—The name *ammonium* is assigned to the radical NH_4 , supposed to be present in the so-called *ammonium-amalgam*.¹ This substance was first prepared by Sebeck by electrolyzing ammonium salts in contact with mercury, and later by Berzelius and Pontin. Ampère regarded ammonia as the oxide of a metallic-like substance related to the alkalies.²

The name ammonia is probably derived from $\delta\mu\mu\sigma$, sand.³ The "hammoniacus sal" mentioned by Pliny⁴ was probably rock-salt, and not the modern sal ammoniac, similar terms being employed by Serapion and Avicenna in the eleventh century. Geber applied the name *sal ammoniacum* or *sal armoniacum* to ammonium chloride, and from the thirteenth to the seventeenth century these names were employed, as well as the name *sal arménacus*. The term *sal ammonia cus* seems to have been definitely applied to ammonium chloride from the eighteenth century onwards. The confusion in nomenclature probably arose through the introduction of ammonium chloride into Europe from Asia about the eighth century under the name *Armenian salt*, this title being later confused with the name *sal ammoniacum* applied to rock salt.

Geber's method for preparing ammonium chloride consisted in evaporating urine with sodium chloride, and subliming the residue. The Egyptians prepared it by subliming the soot formed by the combustion of camels' dung. It was first produced from hydrogen chloride and ammonia by Angelus Sala in 1620, and its qualitative composition was established by Glauber in 1648.

In 1595 Libavius obtained crystals of ammonium sulphate by impure sulphuric acid, and also by evaporating urine with sulphuric acid. It was investigated by Glauber, and received the name *sal ammoniacum secretum Glauberi*. At the close of the seventeenth century it was much in favour as a medicine. Glauber also prepared

¹ See this series Vol III.

Compare Kopp *Geschichte der Chemie* Brunswick, 1845 3 250

² Compare Treumann *Chem Zeit* 1909 33 49 Schone *ibid* 77 von Lippmann *ibid* 117 186 Kout *ibid* 297 Schramm *ibid* 529

³ Pliny *Naturalis Historiae*, Lugdini Batavorum, Rotterdam (Hackios), 1668 Vol 3 Book 31, Chap 7, p 365

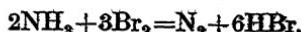
PREFACE

thesis, which, the longer I contemplate, the more I am convinced of its truth. Enough is already done to enable any one to form a judgment of it. The facts and observations yet in reserve, are only of the same kind as those already advanced, if the latter are not sufficient to convince, the addition of the former will be but of little avail. In the mean time, those who, with me, adopt the system, will, I have no doubt, find it a very useful guide in the prosecution of all chemical investigations.

In the arrangement of the articles treated of, I have endeavoured to preserve order, namely, to take such bodies as are simple, according to our present knowledge, and next, those bodies that are compounds of two elements, but in this I have not always succeeded. For, in some instances, it has not been quite clear what was simple, and what compound, in others, the compounds of three or more elements have been so intimately connected with those of two, that it was found impracticable to give a satisfactory account of the latter, without entering more or less into a description of the former.

In regard to nomenclature, I have generally adopted what was most current, perhaps, in a few instances, my peculiar views may have led me to deviate from this rule. I have called those salts *carbonates*, which are constituted of one atom of carbonic acid united to one of base, and the like for other salts. But some moderns call the *neutral* salts *carbonates*, and the former *subcarbonates* whereas, I should call the neutral carbonates of soda and potash *supercarbonates*, consisting of two atoms of acid and one of base. I have, however, continued to call the common *nitrates* by that name, though most of them must be considered on my system as *supernitrates*. I am not very anxious upon this head, as it is evident that if the system I proceed upon be adopted, a general reformation of nomenclature will be the consequence, having a reference to the number of atoms, as well as to the *kind of elements*, constituting the different

of bromine on ammonium salts furnishes a means of comparing the extent of their hydrolytic dissociation. Under certain conditions the action on free ammonia is represented by the equation



and for the ammonium salts its velocity increases with the hydrolytic dissociation.¹ Other methods of determining the degree of hydrolysis have also been devised.²

Ammonium ion and Valency—Although no direct measurement of the electroaffinity of the ammonium ion has been possible, the slight tendency to hydration of its salts indicates that it is stronger than the potassium ion. It is colourless, and the *migration-velocity* at 18° C³ is given as 64.2, and at 25° C⁴ as 73. Like the alkali-metals, the radical ammonium is univalent, and forms salts with one equivalent of an acid

AMMONIUM SALTS

Ammonium fluoride, NH₄F—The fluoride is formed by the interaction of gaseous hydrogen fluoride and anhydrous ammonia. It can be prepared by sublimation from a mixture of ammonium chloride and sodium fluoride.⁵ It forms very brittle, colourless, hexagonal laminae⁶ of strongly saline taste. In dry air it is stable at ordinary temperature. When heated, it fuses, and then sublimes. The dry salt can absorb ammonia at ordinary temperature, the gas being expelled by heat. It is deliquescent, and dissolves in its own weight of water at 0° C.⁷ In aqueous solution it undergoes extensive hydrolytic dissociation. In consequence of the presence of free hydrogen fluoride, the solution attacks glass, and should be stored in vessels made of platinum, silver, or gutta-percha.⁸ Explosive, oily drops of nitrogen fluoride are said to be formed by its electrolysis,⁹ but the statement lacks confirmation.⁷ It is employed as a disinfectant in the brewing industry,¹⁰ and is a powerful preservative, almost inhibiting the fermentation of invert-sugar.¹¹

The heat of formation of the solid from gaseous ammonia and hydrogen fluoride is 37.3 Cal., and the heat of neutralization of the acid by ammonia in aqueous solution is 15.2 Cal.¹²

Ammonium hydrogen fluoride, NH₄F·HF—Evaporation of a solution of the normal salt at a temperature between 36° and 40° C expels ammonia, the primary salt crystallizing out. It can also be prepared by the action of ammonia on a solution of hydrogen fluoride, a small proportion of ammonium sulphide or carbonate being added.¹³ It forms colourless rhombic prisms, readily soluble in water,⁶ with a density of 1.211¹⁴ at 12° C.

¹ Ostwald and Raich *Zeitsch physikal Chem* 1888 2 125

Compte Veley *Trans Chem Soc* 1905 87 26 Hill *ibid* 1906 89 1273
Naumann und Ruckel *J prakt Chem*, 1905, [2] 74 249 Naumann und Muller *ibid* 215 Crossmann *Zeitsch anorg Chem* 1902 33 149

² Kohlrausch und Holborn *Leitfähigkeiten der Elektrolyte* Leipzig 1898

³ Bredig *Zeitsch physikal Chem* 1894 13 228

Berzelius *Lehrbuch der Chemie* 6th ed Leipzig 1866 3 282

⁴ Marignac *Ann Mines* 1859 [o] 15 221 Ruff and Geissel *Ber* 1903 36 26 7

⁵ Rose *Pogg Annalen* 1859 108 19 ⁶ Warren *Chem News* 1887 55 289

¹⁰ Will und Braun *Zeitsch ges Brau* 1904 27 521 537 553

¹¹ Luhing und Saitou *Pharm Zentralhalle* 1908 49 934

¹ Guntz *Compt rend*, 1883 97 1483 *Ann Chim Phys* 1884 [6] 3 5 17

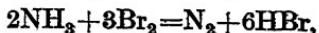
¹² Rose *loc cit*

¹⁴ Bodeker, *Beziehungen zwischen Dichte und Zusammensetzung* Leipzig, 1860

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of bromine on ammonium salts furnishes a means of comparing the extent of their hydrolytic dissociation. Under certain conditions the action on free ammonia is represented by the equation



and for the ammonium salts its velocity increases with the hydrolytic dissociation.¹ Other methods of determining the degree of hydrolysis have also been devised.²

Ammonium ion and Valency — Although no direct measurement of the electroaffinity of the ammonium ion has been possible, the slight tendency to hydration of its salts indicates that it is stronger than the potassium ion. It is colourless, and the *migration-velocity* at 18° C³ is given as 64.2, and at 25° C⁴ as 73. Like the alkali-metals, the radical ammonium is univalent, and forms salts with one equivalent of an acid.

AMMONIUM SALTS

Ammonium fluoride, NH₄F — The fluoride is formed by the interaction of gaseous hydrogen fluoride and anhydrous ammonia. It can be prepared by sublimation from a mixture of ammonium chloride and sodium fluoride.⁵ It forms very brittle, colourless, hexagonal laminae⁶ of strongly saline taste. In dry air it is stable at ordinary temperature. When heated, it fuses, and then sublimes. The dry salt can absorb ammonia at ordinary temperature, the gas being expelled by heat. It is deliquescent, and dissolves in its own weight of water at 0° C.⁷ In aqueous solution it undergoes extensive hydrolytic dissociation. In consequence of the presence of free hydrogen fluoride, the solution attacks glass, and should be stored in vessels made of platinum, silver, or gutta-percha.⁸ Explosive, oily drops of nitrogen fluoride are said to be formed by its electrolysis,⁹ but the statement lacks confirmation.⁷ It is employed as a disinfectant in the brewing industry,¹⁰ and is a powerful preservative, almost inhibiting the fermentation of invert-sugar.¹¹

The heat of formation of the solid from gaseous ammonia and hydrogen fluoride is 37.3 Cal., and the heat of neutralization of the acid by ammonia in aqueous solution is 15.2 Cal.¹²

Ammonium hydrogen fluoride, NH₄F·HF — Evaporation of a solution of the normal salt at a temperature between 36° and 40° C expels ammonia, the primary salt crystallizing out. It can also be prepared by the action of ammonia on a solution of lithium fluoride, a small proportion of ammonium sulphide or carbonate being added.¹³ It forms colourless rhombic prisms, readily soluble in water,⁶ with a density of 1.211¹⁴ at 12° C.

¹ Ostwald and Raich *Zeitsch physikal Chem* 1888 **2** 120

Compton Veley *Trans Chem Soc* 1903, 87 26 Hill *ibid* 1906 89 1273
Naumann und Rucker *J prakt Chem*, 1903 [2] 74 249, Naumann and Müller *ibid* 215 Grossmann *Zeitsch anorg Chem* 1902 33 149

² Kohlhausch and Holborn *Leiternungen der Elektrolyt*, Leipzig 1898

³ Bredig *Zeitsch physikal Chem* 1894 **13** 228

Berzelius *Lärerbuch der Chemie* 6th ed Leipzig, 1856 **3** 282

⁴ Matignac *Ann Mines* 1859 [5] 15 221 Ruff and Geisel *Ber* 1903 36 26 7

⁵ Rose Pogg *Annalen* 1859 108, 19 ⁶ Warren *Chem News* 1887 55 289

¹⁰ Will and Braun *Zeitsch ges Brauw* 1904 27 521 537 553

¹¹ Luhring and Sartori *Pharm Zentralhalle* 1908 49 934

¹² Guntz *Compt rend* 1883, 97 1483 *Ann Chim Phys* 1884 [6] 3 5 17

¹³ Rose *loc cit*

¹⁴ Bodeker, *Beziehungen zwischen Dichte und Zusammensetzung* Leipzig 1860

that any one of the bodies denominated elementary, is absolutely indecomposable, but it ought to be called simple, till it can be analyzed. The principal simple bodies are distinguished by the names *oxygen*, *hydrogen*, *azote* or *nitrogen*, *carbone* or *charcoal*, *sulphur*, *phosphorus*, and the *metals*. The fixed alkalis and the earths were lately undecomposed, but it has long been suspected that they were compounds, and Mr Davy has recently shewn, by means of galvanic agency, that some of them contain metals, and have all the characters of metallic oxides, no harm can arise, it is conceived, therefore, from placing all the earths in the same class as the metallic oxides.

After the elementary or simple bodies, those compounded of two elements require next to be considered. These compounds form a highly interesting class, in which the new principles adopted are capable of being exhibited, and their accuracy investigated by direct experiment. In this class we find several of the most important agents in chemistry, namely, water, the sulphuric, nitric, muriatic, carbonic and phosphoric acids, most of the compound gases, the alkalis, earths, and metallic oxides.

In the succeeding classes we shall find the

A solution in contact with excess of the salt boils at 115.6°C , and at that temperature contains 87.3 grams per 100 grams of water. At 75°C a similar solution contains 38.23 grams of the salt per 100 grams of the solution.¹ In dilute aqueous solution its degree of ionization is of the same order as that of potassium or sodium chloride.²

The volatilization of ammonium chloride by heat is attended by much dissociation³ in presence of moisture, corresponding with 67 to 68 per cent, and a slight decrease in the extent of the dissociation between 280° and 330°C .⁴ Absence of water-vapour almost entirely prevents the dissociation of ammonium chloride, and the combination of hydrogen chloride and ammonia.⁵

The heat of neutralization of ammonia and hydrogen chloride in aqueous solution is given as 12.27 Cal.⁶ and 12.45 Cal.⁷ At ordinary temperature this solution is not absolutely stable.⁸ When heated, it evolves ammonia, and develops an acidic reaction.⁹

When ammonium chloride is heated in contact with air and platinum, there is partial oxidation with formation of nitric acid and liberation of chlorine. Heating the salt with gaseous hydrogen iodide also causes decomposition¹⁰, and heating with potassium forms potassium chloride, with evolution of ammonia and hydrogen. It is also decomposed by other metals. At a red heat it converts many salts and oxides into chlorides,¹¹ but the oxides of cobalt and nickel are reduced to the corresponding metal.¹² At 400°C it reacts with carbonyl chloride, COCl_2 , to form carbamyl chloride, Cl CO NH_2 .¹³ When heated with potassium dichromate, it is decomposed with evolution of nitrogen, nitric oxide, nitrogen peroxide, and chlorine.¹⁴ It combines with ammonia to form complex derivatives,¹⁵ an additive compound prepared by Kendall and Davidson¹⁶ having the formula $\text{NH}_4\text{Cl}, 3\text{NH}_3$, and the melting-point 10.7°C .

Ammonium chloride exerts a catalytic, accelerating effect on certain reactions, examples being the interaction of iodic acid and sulphurous acid,¹⁷ and the inversion of sucrose by hydrochloric acid.¹⁸ It is employed in the manufacture of ammonia and ammonium compounds, in pharmacy and the dye industry, and in soldering.

¹ Tschugaev and Chlopin *Zeitsch anorg Chem*, 1914 86, 154

Noyes, *Zeitsch physikal Chem* 1882 9 608

² Than *Annalen* 1861 131 131 Bineau *Ann Chim Phys*, 1863 [3] 68 416

Ramsay and Young, *Zeitsch physikal Chem* 1887 1 244

⁴ Smith and Lombard *J Amer Chem Soc* 1915 37 38

⁵ Baker *Trans Chem Soc*, 1894 65 611 1898 73, 422, compare Gutmann *Annalen* 1897 299 267

⁶ Thomsen *Thermochemistry* (Longmans, 1908), 115

⁷ Berthelot *Compt rend* 1873 76, 1041 1106

⁸ Leeds, *Chem News*, 1879 39 17 *Amer Chem J* 1880 2, 246 compare Cornwall *ibid* 45

⁹ Watson Smith *J Soc Chem Ind* 1911 30 203 Leeds *Amer J Sci* 1874 [3] 7, 197 *Chem News* 1874 29, 256 *Arch Sci phys nat*, 1874 50 214

¹⁰ Hautefeuille *Bull Soc chim* 1867 [2] 7 198

¹¹ Compare Gmelin Kraut *Handbuch der anorg Chem*, Heidelberg 1872-1897 21 422

¹² Santi *Boll chim farm* 1904 43 673

¹³ Gattermann and Schmidt *Ber* 1887 20 808

¹⁴ Frankforter Roehrich and Manuel *J Amer Chem Soc* 1910 32 176 compare de Luna *Ann Chim Phys* 1863 [3] 68 183

¹⁵ Troost *Compt rend* 1879 88 578

¹⁶ Kendall and Davidson *J Amer Chem Soc* 1920 42 1141

¹⁷ Landolt *Sitzungsber K Akad Wiss Berlin* 1887 21 745

¹⁸ Arrhemus, *Zeitsch physikal Chem* 1889 4 240

be received in phials over water, in the usual way About 30 cubic inches of gas may be expected This gas should be exposed to a mixture of lime and water, which absorbs about $\frac{1}{3}$ of it (carbonic acid), and leaves the rest nearly pure

2 *With the application of heat* Put 2 ounces of manganese (the common black oxide) into an iron bottle, or gun barrel properly prepared, to which a recurved tube is adapted This is then to be put into a fire, and heated red , oxygenous gas will come over, and may be received as before , it usually contains a small portion of carbonic acid, which may be extracted by lime water Three or four pints of air may thus be obtained

3 Two ounces of manganese may be put into a phial, with the same weight of sulphuric acid , the mixture being made into a paste, apply the heat of a candle or lamp, and the gas comes over as before, nearly pure, if taken over water

4 If an ounce of nitre be put into an iron bottle, and exposed to a strong red heat, a large quantity of gas (2 or 3 gallons) may be obtained It consists of about 3 parts oxygen and 1 azote, mixed together

5 Put 100 grains of the salt called oxy-muriate of potash into a glass or earthenware

rivatives,¹ an example being the substance² melting at 13° C., and having the formula $\text{NH}_4\text{Br}_3\text{NH}_3$.

Ammonium iodide, NH_4I .—The iodide is formed by methods analogous to those applicable to the bromide.³ It is also a product of the decomposition of nitrogen iodide in presence of water or ammonium hydroxide.⁴ It is best prepared by addition of alcohol to an aqueous solution of potassium iodide and ammonium sulphate in equimolecular proportions, potassium sulphate crystallizing and ammonium iodide remaining dissolved.⁵ It can also be prepared by the interaction of ferrous iodide and ammonium carbonate, and by that of ammonium hydroxide and iodine in presence of hydrogen peroxide.⁶



Ammonium iodide crystallizes in colourless deliquescent cubes, of density 2.515⁷ at 20° C. For the melting-point Rassow⁸ gives 551° ± 3° C., an accurate determination being prevented by dissociation. Heating causes sublimation, accompanied by almost complete dissociation,⁹ and in presence of air a certain degree of decomposition. The initial effect of heat is to cause the vapour to associate, the degree of association diminishing with rise of temperature.¹⁰ The heat of formation from the elements is 49.31 Cal., and from gaseous ammonia and hydrogen iodide 43.46 Cal.¹¹ At 15° C its solubility is 167 grams in 100 grams of water.¹² In concentrated aqueous solution it is converted by iodine into the tri-iodide,¹³ $\text{NH}_4\text{I}_3\text{I}_2$, tabular, rhombic crystals, isomorphous with the tri-iodides of the alkali-metals.¹⁴ With ammonia, ammonium iodide yields additive compounds.¹⁵ One example is the substance melting at -8.0° C., with the formula $\text{NH}_4\text{I}_3\text{NH}_3$, and another that melting at -5.1° C., with the formula $\text{NH}_4\text{I}_4\text{NH}_3$.

In aqueous solution ammonium iodide is gradually oxidized, the reaction being accelerated by light.¹⁶ The salt finds application in the photographic industry.

Ammonium dichloroiodide, $\text{NH}_4\text{Cl}_2\text{I}$.—The liquid obtained by the action of chlorine on an aqueous solution of ammonium chloride containing iodine in suspension, until the free iodine has just disappeared, deposits scarlet prisms of ammonium dichloroiodide. This perihalide is also formed by the interaction of an aqueous solution of ammonium iodide and chlorine. It is the most stable of the trihalides, and can be

¹ 1100st *Compt rend* 1881 92 715 Roozeboom *Zeitsch physikal Chem* 1888

² 460 *Rec trav chim*, 1885 4 361

Kendall and Davidson *J Amer Chem Soc*, 1920 42 1141

³ Compare Schonbein *J prakt Chem* 1861 84 385

⁴ Guyard *Compt rend* 1883 97 526 *Mon Scient* 1883 [3] 13 1011

⁵ Jacobsen *Neues Jahrb Pharm* 1864 20 91

⁶ Broeksmut, *Pharm Weekblad*, 1917 54 1373 compare Rupp *Apoth Zest*, 1918,

33 406, 473

⁷ Le Blanc and Rohland *Zeitsch physikal Chem* 1896 19 261

⁸ Rassow *Zeitsch anorg Chem* 1920 114 117

⁹ Deville and Troost, *Compt rend* 1859 49 239 1863 56 891 *Annalen* 1860

113 42 1863 127 274

¹⁰ Smith and Lombard *J Amer Chem Soc* 1915 37 38

¹¹ Thomsen, *Thermochemistry* (Longmans, 1908) 251

¹² Edler Dingler's *Polytech J* 1876 221 189

¹³ Johnson *Chem News* 1878 37 270 *Trans Chem Soc* 1878 33 397

¹⁴ Wheeler Barnes and Pratt *Amer Chem J* 1897 19 672

¹⁵ Kendall and Davidson *J Amer Chem Soc*, 1920 42 1141

¹⁶ Leeds, *Pharm J*, 1879, [3], 9, 1017

by 7, that of an atom of hydrogen being 1; this is inferred from the relative weights of those elements entering into combination to form water. The diameter of a particle of oxygen, in its elastic state, is to that of one of hydrogen, as 794 to 1 *

2 Oxygen unites with hydrogen, charcoal, azote, phosphorus, and other bodies denominated combustible, and that in various manners and proportions, when mixed with hydrogen and some other elastic fluids, it explodes by an electric spark, with noise, and a violent concussion of the vessel, together with the extrication of much heat. This is called *detonation*. In other cases, the union of oxygen with bodies is more slow, but accompanied by heat. This is usually called *combustion*, as in the burning of charcoal, and *inflammation*, when accompanied with flame, as in the burning of oil.—In other cases, the union is still more slow, and consequently with

* For, the diameter of an elastic particle is as $\sqrt[3]{}$ (weight of one atom — specific gravity of the fluid). Whence, denoting the weight of an atom of hydrogen by 1, and the specific gravity of hydrogenous gas also by 1, the weight of an atom of oxygen will be 7, and the specific gravity of oxygenous gas, 14, we have then $\sqrt[3]{\frac{7}{14}} = 1$, or $\sqrt[3]{\frac{1}{14}} = 1$, or 794 : 1. diameter of an atom of oxygen : the diameter of one of hydrogen.

composed by heat, slowly between 145° and 150° C, rapidly at 180° C,¹ and is employed in the manufacture of explosives.²

Ammonium hypobromite.—Bromine is said to react with a well-cooled ammonium-hydroxide solution, with formation of an unstable solution of the hypobromite.³

Ammonium bromate, NH_4BrO_3 .—Evaporation of an aqueous solution of ammonia and bromic acid, or of barium bromate and ammonium carbonate, yields the bromate in colourless needles. They are very unstable, and decompose with some energy at ordinary temperatures.⁴

Ammonium hypoiodite—A very unstable solution of the hypoiodite is probably formed by addition of excess of ammonium hydroxide to an aqueous solution of iodine. The solution exerts a powerful bleaching action, but rapidly decomposes into iodine and iodate.⁵

Ammonium iodate, NH_4IO_3 .—The iodate is produced by the action of ammonia or ammonium carbonate on iodic acid or iodine trichloride, and is also one of the products of the interaction of iodine and ammonia.⁶ It forms colourless rhombic⁷ crystals, of density 3.3085⁸ at 21° C, its solubility at 30° C being 4.2 grams in 100 grams of water.⁹ At 150° C. it decomposes energetically into oxygen, nitrogen, iodine, and water.¹⁰ Acid salts derived from one molecule of the iodate and one molecule¹¹ or two molecules¹² of iodic acid have been described.

Ammonium periodate, NH_4IO_4 .—Neutralization of periodic acid with ammonia yields the periodate in tetragonal crystals isomorphous with the corresponding potassium, sodium, and rubidium salts,¹³ and also with the periodates of silver and lithium.¹⁴ Its density at 18° C is 3.056, and its solubility at 16° C is 2.7 grams in 100 grams of water.¹⁵ Several hydrates¹⁶ and complex periodates¹⁷ have been described, examples being $(\text{NH}_4)_2\text{H}_3\text{IO}_6$, prepared by Rammelsberg and Groth,¹⁸ and $(\text{NH}_4)_3\text{H}_7(\text{IO}_6)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$.¹⁹ The hydrated salt with the second formula is obtained in the form of rectangular crystals by agitating periodic acid with excess of 25 per cent ammonia at 140° C for several hours.

¹ Girard and Laroche *Mon Scient* 1909, [4], 23, 1, 217

² Alvisi, *Gazzetta* 1899, 29, 1, 121

³ Maumené *Compt rend* 1870, 70, 147 Kraut *Gmelin Kraut's Handbuch der anorg Chem*, Heidelberg, 1872-1897, 2, 1, 560 Foster, *Trans Chem Soc* 1886, 33, 470 Bosetti *Arch Pharm* 1889, [3], 27, 120

⁴ Rammelsberg *Pogg Annalen* 1833, 52, 85 compare Rötgers *Zeitsch physikal Chem* 1890, 5, 436

⁵ Compare Gmelin Kraut *Handbuch der anorg Chem*, Heidelberg 1872-1897, 2, 1, 289, 495

⁶ Gmelin Kraut *ibid* Guyard, *Compt rend* 1883, 97, 326 *Mon Scient* 1883, [3], 13, 1011

⁷ Lakle *Zeitsch Kyst Min*, 1896, 26, 508, Ries *ibid* 1905, 41, 243

⁸ Clarke *Amer J Sci* 1877, [3], 14, 281

⁹ Meerburg *Zeitsch anorg Chem* 1905, 45, 324

¹⁰ P. *ibid* P. *ibid* *Annalen*, 1838, 44, 555

¹¹ P. *ibid* P. *ibid* *Phys* 1890, [6], 21, 146

¹² Meerburg *loc cit* Blomstrand *J prakt Chem* 1889, 40, 338

¹³ Barker *Trans Chem Soc*, 1908, 93, 15

¹⁴ Rammelsberg *Pogg Annalen* 1868, 134, 368

¹⁵ Barker *loc cit*

¹⁶ Eakle *Zeitsch Kyst Min* 1896, 26, 558 Ihre *Ber* 1876, 9, 316 Langlois *Ann Chem Phys* 1852, [3], 34, 257 *Annalen* 1852, 83, 153

¹⁷ Ihle *loc cit* Rammelsberg and Groth *Pogg Annalen* 1868, 134, 379

¹⁸ Rammelsberg and Groth, *loc cit* compare Rosenheim and Loewenthal *Kolloid Zeitsch*, 1919, 25, 53

¹⁹ Rosenheim and Loewenthal *loc cit*

per cent oxygenous gas, the air expired, usually contains about 17 per cent oxygen, and 4 carbonic acid. But if a full expiration of air be made, and the last portion of the expired air be examined, it will be found to have 8 or 9 per cent carbonic acid, and to have lost the same quantity of oxygenous gas.

4 Oxygenous gas is not sensibly affected by continually passing electric sparks or shocks through it, nor has any other operation been found to decompose it.

SECTION 2

HYDROGEN

Hydrogenous gas may be procured by taking half an ounce of iron or zinc filings, turnings, or other small pieces of these metals, putting them into a phial, with two or three ounces of water, to which pour one quarter as much sulphuric acid, and an effervescence will be produced, with abundance of the gas, which may be received over water in the usual way.

Some of its distinguishing properties are —

1 It is the lightest gas with which we are acquainted. Its specific gravity is nearly 0805, that of atmospheric air being 1. This

and readily decomposed into ammonia and ammonium hydrogen sulphide. Bloxam¹ regards the ordinary solution of ammonium sulphide as $(\text{NH}_4)_2\text{S} + 2\text{NH}_4\text{SH} + 2\text{NH}_4\text{OH}$. Several complex derivatives with ammonia have been described.² The heat of formation of the sulphide from ammonia and hydrogen sulphide in aqueous solution is given as 6.2 Cal³ and 6.3 Cal⁴.

Ammonium hydrogen sulphide, NH_4SH —The primary sulphide is formed in white crystals by the interaction of ammonia and hydrogen sulphide in ethyl-acetate solution⁵. At or below 0° C it undergoes only a slow decomposition into hydrogen sulphide and ammonia. Its melting-point in a closed vessel is 120° C⁶. Its heat of formation from sulphur-vapour, hydrogen, and nitrogen has been calculated⁷ to be 42.4 Cal. In aqueous solution it undergoes extensive hydrolytic dissociation, and the strongly alkaline solution is oxidized by exposure to air, yielding a yellow solution containing polysulphides and also sulphite and thiosulphate⁸. This liquid constitutes the ordinary solution of ammonium sulphide employed in analysis, it can also be prepared by dissolving sulphur in a solution of ammonium hydrogen sulphide, or by distilling a hot solution of sodium sulphide and ammonium chloride.⁹

The so called "volatile liver of sulphur" is a mixture of ammonium hydrogen sulphide and polysulphides, and is obtained as a dark-red, fuming liquid by distilling ammonium chloride, sulphur, and lime.¹⁰

Ammonium polysulphides—Various solid polysulphides have been described,¹¹ but there is no certainty that they are true compounds. Examples are the *tetrasulphide*, $(\text{NH}_4)_2\text{S}_4$, unstable yellow crystals prepared by cooling the mother-liquor of the pentasulphide after treatment with hydrogen sulphide and ammonia, and along with pentasulphide by the action of these reagents on a solution of the enneasulphide, the *pentasulphide*, $(\text{NH}_4)_2\text{S}_5$, rhombic orange crystals obtained by dissolving sulphur in a warm solution containing hydrogen sulphide and ammonia in the ratio 1:2, or by addition of alcohol to a cold concentrated solution of ammonium sulphide saturated with sulphur¹², the *heptasulphide*, $(\text{NH}_4)_2\text{S}_7$,¹³ ruby-red crystals produced by dissolving the pentasulphide in its own mother-liquor and allowing the solution to crystallize, or as crystals of violet lustre and the formula $3(\text{NH}_4)_2\text{S}_7 \cdot 4\text{H}_2\text{O}$ by saturating a concentrated solution of ammonia with hydrogen sulphide and sulphur, and the *ennenasulphide*, $(\text{NH}_4)_2\text{S}_9 \cdot \frac{1}{2}\text{H}_2\text{O}$, deep red crystals deposited from the mother-liquor of the pentasulphide after prolonged exposure to air.

¹ Bloxam *Zeitsch. anorg. Chem.* 1908 60 113

Bloxam, *Chem. News* 1893 68 97 Maumenee *Compt. rend.* 1879 89 506

Berthelot *Ann. Chim. Phys.* 1875 [5] 4 187

⁴ Thomsen *Thermochemische Untersuchungen* Leipzig 1882-1883, I 264

⁵ Naumann *Bei.* 1910 43 313 compare Tiöst *Compt. rend.* 1879 88 1267

⁶ Briner *Compt. rend.* 1906 142 1416

⁷ Berthelot *ibid.*, 1880 90 779 *Ann. Chim. Phys.* 1880 [5] 20 255

⁸ Bloxam *Chem. News* 1893 68 97 *Trans. Chem. Soc.* 1893 67 277

⁹ Donath *Chem. Zeit.* 1891 15, 1021

¹⁰ Gay Lussac *Pogg. Annalen* 1829 15 538 *Ann. Chim. Phys.* 1829 40 302

Vauquelin *ibid.* 1817 6 42

¹¹ Fritzsche *J. prakt. Chem.*, 1841 24 460 1844 32 313 Bloxam *Trans. Chem. Soc.* 1895 67 277

¹² Byers *Amer. Chem. J.* 1902 28 490

¹³ Fritzsche's heptasulphide is regarded by Sabatier (*Ann. Chim. Phys.* 1881 [5] 22 73) as an octasulphide, $(\text{NH}_4)_2\text{S}_8$

stantly condensed into water When 2 measures of hydrogen are mixed with 1 of oxygen, and exploded over water, the whole gas disappears, and the vessel becomes filled with water, in consequence of the formation and subsequent condensation of the steam

If 2 measures of atmospheric air be mixed with 1 of hydrogen, and the electric spark made to pass through the mixture, an explosion ensues, and the residuary gas is found to be $1\frac{3}{4}$ measures, consisting of azote and a small portion of hydrogen The portion of the mixture which disappears, $1\frac{1}{4}$, being divided by 3, gives 42 nearly, denoting the oxygen in two measures of atmospheric air, or 21 per cent The instrument for exploding such mixtures is called *Volta's eudiometer*

5 Another remarkable property of hydrogen deserves notice, though it is not peculiar to it, but belongs in degree to all other gases that differ materially from atmospheric air in specific gravity, if a cylindrical jar of 2 or more inches in diameter, be filled with hydrogen, placed upright and uncovered for a moment or two, nearly the whole will vanish, and its place be supplied by atmospheric air In this case it must evidently leave the vessel in a body, and the other enter in the same manner But if the jar of hydrogen be held with its

and of coke in coke-ovens, furnishes the main bulk of the world's supply of ammonium sulphate. Most of the ammonia is dissolved in the condensed aqueous vapour obtained by cooling the gas, and the residual portion is extracted by washing with water. In coke-works the ammonia is sometimes absorbed from the hot gas by means of sulphuric acid, after the removal of the tar.

The free ammonia in the aqueous solution is expelled by heat, and absorbed by sulphuric acid in a lead saturator, and the fixed ammonia is then liberated by lime, and similarly absorbed.

In Woltereck's process for the manufacture of ammonia from peat,¹ carried on at Carnlough in the north of Ireland, the wet peat is burnt in air and steam at a low temperature. After the tar produced has been washed out by oils of high boiling point, and the acetic acid removed by hot milk of lime, the ammonia is absorbed by sulphuric acid.

The sulphate crystallizes in transparent rhombic crystals,² isomorphous with those of potassium sulphate. The effect of various impurities on the colour of the salt has been investigated by Leo.³ The literature contains many contradictory statements respecting the melting-point of ammonium sulphate and the behaviour of the substance under the influence of heat. According to Marchand,⁴ the melting-point is 140° C., but Watson Smith⁵ and Caspar⁶ regard this temperature as the melting-point of the primary sulphate. Watson Smith⁷ states that ammonium sulphate begins to evolve ammonia at 100° C., and at 300° C. is completely converted into the primary sulphate. According to Caspar,⁸ in an open tube the normal sulphate softens at 310° C., melts at a temperature between 386° and 390° C., and decomposes with evolution of gas at 355° C., in a closed tube at 365° C. Janecke⁹ states that both the normal sulphate and the primary sulphate melt at 251° C., but in a later paper¹⁰ gives 147° C. as the melting-point of the primary sulphate. The explanation of these very divergent values is to be found in the observation by Kendall and Davidson¹¹ of the impossibility of determining in an open tube the true melting-point of the normal sulphate, owing to loss of ammonia even at 200° C. When the salt is heated in a sealed tube almost filled, it softens at 490° C. and melts at 513° + 2° C., the value given representing the melting point of the substance at an ammonia pressure of considerably more than one atmosphere. When the salt is heated in an open tube, decomposition is complete at 365° C.¹¹

Janecke's⁸ value for the boiling point of the normal sulphate, 357° C., does not accord with the work of Kendall and Davidson¹². The

¹ Woltereck *British Patents*, 1904 No 16504 1906 Nos 28963 and 28964

² Mitscherlich *Pogg Annalen* 1830 18, 168 Tutton, *Trans Chem Soc* 1903 83
1049 *Zeitsch Kryst Min* 1905 41 525

³ Leo *Stahl und Eisen* 1914 34 439

⁴ Marchand *Pogg Annalen* 1837 42 556

⁵ Watson Smith *J Soc Chem Ind*, 1911 30 253 compare Reik *Monatsh* 1902

²³ 1033

⁶ Caspar *Ber* 1920 53 [B], 821

⁷ Watson Smith *loc cit*

⁸ Janecke *Zeitsch angew Chem* 1920 33 278

⁹ Janecke, *ibid* 1921 34 542

¹⁰ Kendall and Davidson, *J Ind Eng Chem* 1921 13 303 compare Kendall and Landon, *J Amer Chem Soc*, 1920 42 2131 Kattwinkel *Ber* 1922 55 [B] 874

¹¹ Kattwinkel, *loc cit*

¹² Kendall and Davidson *loc cit*

100 measures of atmospheric air put 30 of nitrous gas, the mixture having stood some time, must be passed two or three times through water, it will still contain a small portion of oxygen, to the residuum put 5 more measures of nitrous gas, and proceed as before, small portions of the residuum must then be tried separately, by nitrous gas and by atmospheric air, to see whether any diminution takes place, whichever produces a diminution after the mixture, shews that it is wanting, and the other redundant, consequently a small addition to the stock must be made accordingly By a few trials the due proportion may be found, and the gas being then well washed, may be considered as pure azotic 2 If a quantity of liquid sulphuret of lime (a yellow liquid procured by boiling one ounce of a mixture of equal parts sulphur and lime in a quart of water, till it becomes a pint) be agitated in 2 or 3 times its bulk of atmospheric air for some time, it will take out all the oxygen, and leave the azotic gas pure 3 If to 100 measures of atmospheric air 42 of hydrogen be put and an electric spark passed through the mixture, an explosion will take place, and there will be left 80 measures of azotic gas, &c

The properties of this gas are,—

1 The specific gravity of azotic gas at the

Ammonium hydrogen sulphate, NH_4HSO_4 —On cooling a saturated solution of the normal sulphate in concentrated sulphuric acid, the primary sulphate is deposited in deliquescent, rhombic prisms.¹ It is also produced by heating the normal salt.² For the melting-point of the primary sulphate,³ Watson Smith⁴ gives 140° C , but more reliance can be placed on the value $146.9^\circ \pm 0.5^\circ \text{ C}$ of Kendall and Landon⁵ and on that (147° C) of Janecke.⁶ For the boiling-point, Janecke⁷ gives 490° C . The density of the primary sulphate is given as 1.787⁸ and 1.815⁹. It is soluble in an equal weight of water.¹⁰ Several other acid sulphates have been described,¹¹ such as $(\text{NH}_4)_2\text{SO}_4 \cdot 3\text{H}_2\text{SO}_4$, melting at 48° C .¹² An ammonia compound, $(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{NH}_3$, has also been prepared.¹³

Ammonium pyrosulphate, $(\text{NH}_4)_2\text{S}_2\text{O}$ —Sulphur trioxide combines with ammonium sulphate with evolution of heat, yielding the pyrosulphate as an amorphous, translucent, deliquescent substance, rendered crystalline by fusing and allowing to solidify. Its melting-point is given as 138° C .¹⁴ The primary sulphate crystallizes from its solution.¹⁵

An octasulphate, $(\text{NH}_4)_2\text{O}_8\text{S}_2\text{O}_3$, has also been described.¹⁶

Ammonium persulphate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ —The persulphate is produced at the anode in the electrolysis of a cooled saturated solution of ammonium sulphate in dilute sulphuric acid, a high anodic current-density and a diaphragm being employed.¹⁶ It can also be prepared technically without a diaphragm.¹⁷ It forms monoclinic crystals,¹⁸ its solubility at 0° C being 58 grams in 100 grams of water,¹⁹ and greater than that of any other persulphate.²⁰ If free from moisture and protected from sunlight the dry salt scarcely undergoes any change.

When warmed with nitric acid it evolves O_2 .

than the corresponding salts of sodium and potassium, the reaction affording a method of preparing this gas.²² It converts metallic oxides into persulphates, peroxides, or sesquioxides, with evolution of ammonia.²³

¹ Marignac *Ann. Mines*, 1857 [5], 12 38

² Watson Smith *J. Soc. Chem. Ind.* 1911, 30, 253, compare Reik *Monatsh.* 1902 23, 1033

³ Compare the section on normal ammonium sulphate

⁴ Watson Smith *loc. cit.*

⁵ Kendall and Landon *J. Amer. Chem. Soc.* 1920, 42 2131 compare Kendall and Davidson *J. Ind. Eng. Chem.* 1921, 13, 303

⁶ Janecke *Zeitsch. angew. Chem.* 1921, 34, 542, compare however Janecke, *ibid.* 1920, 33 278

⁷ Janecke *ibid.* 1920, 33, 278

⁸ Schiff *Annalen* 1858 107 83

⁹ Gossner *Zeitsch. Kryst. Min.* 1904, 39 381

¹⁰ Link *Crelle's chem. Ann.* 1796, 1, 26

¹¹ Mitscherlich *Pogg. Annalen* 1836, 39 195 *Ann. Mines* 1857 [5] 12 38 (but compare Schiff, *Annalen* 1858 107 83 Johnson and Clittenden *Trans. J. Sci.* 1878 [3] 15 131) *d. Ans. Zeitsch. anorg. Chem.* 1913, 80 235

¹² Kendall and Landon *loc. cit.* Janecke *Zeitsch. angew. Chem.* 1921, 34 342

¹³ Janecke *loc. cit.*

¹⁴ Schulze *Ber.* 1884, 17, 2705

¹⁵ Weber *ibid.* 2497

¹⁶ Berthelot *Compt. rend.* 1892, 114 876 Elbs *J. prakt. Chem.* 1893 [2] 48 185

¹⁷ Mülleit and Friedberger *Zeitsch. Elektrochem.* 1902, 8, 230 Konsortium für elektrochemische Industrie German Patent 1908 No 195811

¹⁸ Fock *Zeitsch. Kryst. Min.* 1893, 22 29

¹⁹ Marshall *Trans. Chem. Soc.* 1891, 59 777

²⁰ Elbs and Schonherr *Zeitsch. Elektrochem.* 1894, 1, 417, 468 1895, 2 162 245

²¹ Elbs and Neher, *Chem. Zeit.* 1921, 45 1113

²² Malaquin *J. Pharm. Chim.* 1911 [7] 3 329

²³ Seyewitz and Trawitz *Compt. rend.* 1903, 137, 130

diffused through the former, and this mixture constitutes the principal part of the atmosphere, and is suited, as we perceive, both for animal life and combustion

5 Azotic gas is not affected by repeated electrification

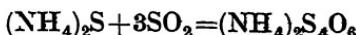
SECTION 4

ON CARBONE OR CHARCOAL

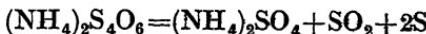
If a piece of wood be put into a crucible, and covered with sand, and the whole gradually raised to a red heat, the wood is decomposed, water, an acid, and several elastic fluids are disengaged, particularly carbonic acid, carburetted hydrogen, and carbonic oxide. Finally, there remains a black, brittle, porous substance in the crucible, called *charcoal*, which is incapable of change by heat in close vessels, but burns in the open air, and is converted into an elastic fluid, carbonic acid. Charcoal constitutes from 15 to 20 per cent of the weight of the wood from which it was derived.

Charcoal is insoluble in water, it is without taste or smell, but contributes much to correct putrefaction in animal substances. It is less liable to decay than wood by the action of air.

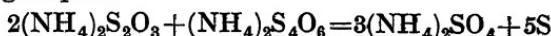
Ammonium tetrathionate, $(\text{NH}_4)_2\text{S}_4\text{O}_6$ —The tetrathionate is produced by the action of sulphur dioxide on an aqueous solution of ammonium sulphide ¹



In aqueous solution it decomposes in accordance with the equation ²



Ammonium thiosulphate reacts with it, forming ammonium sulphate and liberating sulphur



Ammonium selenide, $(\text{NH}_4)_2\text{Se}$ —Excess of ammonia reacts with hydrogen selenide to form ammonium selenide as a white mass ³. It is also produced in the form of black, orthorhombic crystals by concentrating in vacuum over sulphuric acid an aqueous solution of ammonium molybdate and ammonia saturated with hydrogen selenide, the dark colour being probably due to slight decomposition ⁴. On exposure to air it gradually decomposes, with liberation of black selenium. It dissolves in water, forming a red solution from which metallic salts precipitate the corresponding selenide. Its heat of formation from its elements in dilute solution is 44.6 Cal ⁵.

Ammonia unites with excess of hydrogen selenide to form *ammonium hydrogen selenide*, NH_4SeH , the heat of formation of the solid compound from its elements being 28.9 Cal ⁵.

Ammonium selenite, $(\text{NH}_4)_2\text{SeO}_3$ —Concentration of an alcoholic or aqueous solution of selenious acid saturated ⁶ selenite in four-sided columns or laminæ ⁶. Or with separation of selenium, and evolution of nitrogen.

Ammonium selenates—On evaporation, a solution of selenic acid saturated with ammonia yields the *normal selenate*, $(\text{NH}_4)_2\text{SeO}_4$, in monoclinic ⁷ crystals. At 7° C its solubility is 117 grams in 100 grams of water ⁸. When gently heated, the normal salt is converted into *ammonium hydrogen selenate*, NH_4HSeO_4 , of density 2.162 ¹⁰.

Several complex selenate derivatives have been described ¹¹.

ISOMORPHISM OF THE ALKALI-METAL SULPHATES AND SELENATES

The normal sulphates and selenates of the alkali metals, $R_2[\text{Se}]O_4$ where R represents potassium, rubidium, or cesium, form excellent crystals belonging to the rhombic system, and these salts furnish one

¹ Hurdelbunk *J Gasbeleuchtung* 1910 53 956

² Paepe *Bull Soc chim* 1912 26 244

³ Bineau, *Ann Chim Phys* 1838 67 230 68 430 1839 70 261

⁴ Lenher and Smith *J Amer Chem Soc* 1898, 20 277

⁵ Fabre *Compt rend* 1886 103 269

⁶ Muspratt *Annalen* 1849 70 275

⁷ Topsoe *Sitzungsber K Akad Wiss Wien*, 1872 66 18 Retgers *Zeitsch physikal Chem* 1891 8 6 Tutton *Trans Chem Soc* 1906 89 105 compare Ing Situng ber K Akad Wiss Wien, 1862 45 108 Rammelsberg, *Handbuch der Kristallographisch Physikalischen Chemie*, Leipsic, 1881-1882 1, 497

⁸ Tutton *loc cit*

⁹ Cameron and Davy *Chem News*, 1878 38 133

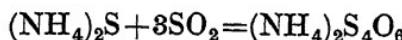
¹⁰ Topsoe *loc cit*

¹¹ Retgers, *loc cit*, Weinland and Bartlingck *Ber* 1903 36 1397 On ammonium tellurate compare Lenher and Wolensky *J Amer Chem Soc*, 1913 35, 718

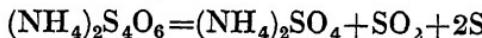
peared an increase of weight of 6 or 7 grains, from the acid mingling with the common air in the flask, of less specific gravity, but the succeeding increase was not more than 6 grains, and arose from the moisture which permeated the bladder for the bladder continued as distended as at first, and finally upon examination was found to contain nothing but atmospheric air Yet carbonic acid is stated to be the most absorbable by charcoal One of the authors above alluded to, asserts that the heat of boiling water is sufficient to expel the greater part of the gases so absorbed Now this is certainly not true, as Allen and Pepys have shewn, and most practical chemists know that no air is to be obtained from moist charcoal below a red heat Hence the weight acquired by fresh made charcoal, is in all probability to be wholly ascribed to the moisture which it absorbs from the atmosphere, and it is to the decomposition of this water, and the union of its elements with charcoal, that we obtain such an abundance of gases by the application of a red heat

It was the, v. opinion some time ago that charcoal was an oxide of diamond, but Mr Tennant, and more recently Messrs Allen and Pepys, have shewn that the same quantity of carbonic acid is obtained from the

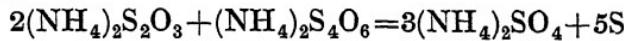
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¹ Huidelbink *J Gasbeleuchtung* 1910 53 96

Paepe *Bull Soc chim* 1912 26 244

² Bineau *Ann Chim Phys* 1838 67 230 68 435 1859 70 261

³ Lenher and Smith *J Amer Chem Soc* 1898, 20 277

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⁴ Muspratt *Annalen* 1849 70 275

Topsoe *Sitzungsber K Akad Wiss Wien*, 1872 66 18 Peter *Z. physikal Chem* 1891 8 6 Tutton *Trans Chem Soc* 1906 89 1059 compare *Sitzung Ber K Akad Wiss Wien* 1862, 45 108 Rammelsberg *Handbuch der Kristallographisch Physikalischen Chemie* Leipzig 1881-1882 I 497

⁵ Tutton *loc cit*

⁶ Cameron and Davy *Chem News* 1878 38 133

⁷ Topsoe *loc cit*

⁸ Retgers *loc cit* Weinland and Bartlingck *Ber* 1903 36 1397 On ammonium tellurate compare Lenher and Wolensky *J Amer Chem Soc* 1913 35 718

SECTION 5

ON SULPHUR

Sulphur or brimstone is an article well known, it is an element pretty generally disseminated, but is most abundant in volcanic countries, and in certain minerals A great part of what is used in this country is imported from Italy and Sicily, the rest is obtained from the ores of copper, lead, iron, &c

Sulphur is fused by a heat a little above that of boiling water It is usually run into cylindrical molds, and upon cooling becomes *roll* sulphur In this case the rolls become highly electrical by friction they are remarkably brittle, frequently falling in pieces by the contact of the warm hand Its specific gravity is 1 98 or 1 99

Sulphur is sublimed by a heat more than sufficient to fuse it, the sublimate constitutes the common *flowers* of sulphur The effects of the different gradations of heat on sulphur are somewhat remarkable It is fused at 226° or 228° of Fahrenheit, into a thin fluid, it begins to grow thick, darker, and viscid at about 350°, and continues so till 600° or upwards, the fumes becoming gradually more

in atomic number in passing from potassium to rubidium and thence to caesium means the addition of a complete shell of electrons to the structure of the atom of the alkali-metal according to the Lewis-Langmuir version of the atomic-structure theory, or of two complete shells according to the Bohr-Sommerfeld version. It has also been shown by W L Bragg that these three alkali-metals occupy the positions corresponding with the sharp maxima of the curve of atomic diameters, which expresses the size of the chemical atoms as revealed in the accumulated results of X-ray analyses of crystals, and that there is a considerable increase in the size of the atom from potassium to rubidium, and again from rubidium to caesium, corresponding with this addition of electrons in one or two shells.

All Tutton's investigations fully confirm one another in the details of the measurements of both exterior angles and of interior physical constants. Their main results may be summarized in the statement that the progression in the atomic-sequence number, and its attendant progression in the size of the atom, is accompanied by a similarly definite progression in the characters, external or internal, of the crystals of these isomorphous rhombic and monoclinic series, when the potassium in the initial salt of the series is replaced by rubidium, and the rubidium in turn replaced by caesium. This fact has been proved definitely for the interfacial angles, for the axial ratios, for the variable axial angle of the monoclinic series, for the relative volumes and edge-dimensions of the rhombic or monoclinic cells of the structural space-lattices, for the refractive indices and molecular refractions, for the amount of double refraction, for the orientation of the optical ellipsoid of the monoclinic series, which is free to rotate about the symmetry-axis, and does so progressively, for the thermal expansions of the rhombic sulphates, which alone were suitable for dilatation experiments, and finally, by the X-ray analysis of the sulphates by Sir William Bragg's X-ray spectrometer for the absolute dimensions of the space-lattice cells, Tutton's relative measures having been found correct to 1 in 1000.

Another ~~CARTESIUS IN~~ has also penetrated to the depths of deeper than was at first appreciated. The ammonium salts are almost perfectly isostructural with the rubidium salts, the replacement of rubidium atoms by ammonium (NH_4) radicals involving practically no change in the relative dimensions of the structural cell edges. This result also has been confirmed fully by the absolute determinations by X rays for rubidium and ammonium sulphates. It follows that the valency-volume theory of Pope and Barlow is incorrect, since according to that theory the relative volumes of rubidium sulphate and ammonium sulphate should be as 1 to 2, the valency volumes being 12 and 24 respectively. The subsequent discovery of the law of atomic diameters from the results of X-ray analyses has decided the matter by showing that size of atom is involved, but that the sizes are not proportional to the valencies and are those expressed in the curve and table of atomic diameters of W L Bragg.

Tutton's main law of progression of the crystallographic properties of the salts of these isomorphous series with the atomic number of the interchangeable alkali metal is in complete agreement with this law of atomic diameters, and the two laws may be said mutually to support each other. To go even deeper, however, the law of progression of the

essential in sulphur, is derived from the consideration of the low specific heat of sulphur. If this article contained 7 or 8 per cent of hydrogen, or 50 per cent of oxygen, or as much water, it would not have the low specific heat of 19.

Sulphur burns in the open air at the temperature of 500° , it unites with oxygen, hydrogen, the alkalis, earths and metals, forming a great variety of interesting compounds, which will be considered in their respective places.

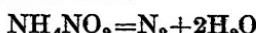
SECTION 6

ON PHOSPHORUS

Phosphorus is an article having much the same appearance and consistency as white wax. It is usually prepared from the bones of animals, which contain one of its compounds, phosphate of lime, by a laborious and complex process. The bones are calcined in an open fire, when reduced to powder, sulphuric acid diluted with water is added, this acid takes part of the lime, and forms an insoluble compound, but detaches superphosphate of lime, which is soluble in water. This solution is evaporated, and the salt is obtained in a glacial state. The solid is reduced to powder, and

can also be produced by the action of nitrogen peroxide on ammonium carbonate, extracting the product with absolute alcohol, and precipitating the nitrite with ether¹, and by a similar precipitation-method from an aqueous alcoholic solution of sodium nitrite and ammonium sulphate². The methods employed in its preparation have been summarized by Sørensen.¹

Ammonium nitrite crystallizes in deliquescent, feather-like needles with a faint yellowish tinge. Its heat of formation from its elements is 64.8 Cal³. When heated, either in the solid state or in solution, it decomposes into nitrogen and water



For the solid the decomposition takes place between 60° and 70° C., and readily develops an explosive character⁴. It is facilitated by acidifying the nitrite⁵. The pure salt is said to be non-explosive, but to be decomposed in accordance with the equation by heating at 100° C in a Hofmann tube⁶. The salt is comparatively stable when kept beneath a layer of alcohol-free ether

The decomposition of the nitrite in aqueous solution has been the subject of many investigations⁷. In vacuum at 37° to 40° C. the decomposition is very slight, at 70° C it proceeds slowly in accordance with the equation, but most of the salt sublimes unchanged. When the sublimate is heated with a naked flame, it yields nitrogen and up to 6 per cent of nitric oxide⁸.

The decomposition of the nitrite is much accelerated by the catalytic action of platinum-black⁹. Other catalysts are also said to facilitate the reaction¹⁰.

Ammonium nitrate, NH_4NO_3 .—The nitrate can be prepared by the general methods applicable to the ammonium salts. It is also produced by heating the nitrate of an alkali-metal with ammonium sulphate at 160° to 200° C., the fused ammonium nitrate being separated from the solid alkali metal sulphate by centrifuging¹¹. Another method consists in cooling a concentrated solution of sodium nitrate and ammonium sulphate to -15° C., sodium sulphate being precipitated. On evaporation of the mother-liquor, most of the sodium sulphate is deposited, addition of nitric acid to the clear solution causes crystallization of the ammonium nitrate¹². When sodium nitrate is

¹ Sørensen *Zeitsch anorg Chem* 1894 7 1

² Blitz and Gahl *Zeitsch Elektrochem* 1905 11 409

³ Berthelot *Ann Chim Phys*, 1880 [5], 20 255

⁴ Berthelot, *Compt rend* 1874 78 102

⁵ Sørensen *loc cit*

⁶ Neogi and Adhikary *Trans Chem Soc* 1911, 99 116

⁷ Berzelius *Gilbert's Annalen* 1812 40 206 Corenwinder *Ann Chim Phys* 1849 [3] 26 296, Millon *ibid* 1847 [3] 19 255 Bohlig *Annalen* 1863 125 21 Angel and Boeris, *Atti R Accad Lincei* 1892 [5] 1 11 70 *Cavetta* 1892 22 11 349 Wegscheider *Zeitsch physikal Chem* 1901 36, 543 Arndt *ibid* 1902 39 64 1903 45 570 Blanchard *ibid* 1902 41 681 1905, 51 117 Vely *Trans Chem Soc* 1903 83 736 Berger *Bull Soc chim*, 1904, [3] 41, 682, Biltz and Gahl *Zeitsch Elektrochem* 1905, 11 409

⁸ Ray *Trans Chem Soc* 1909 95 345

⁹ Vondráček *Zeitsch anorg Chem* 1904 39 37

¹⁰ Arndt *loc cit* Blanchard *loc cit* Viley *Proc Roy Soc* 1888 44 239 *Phil Trans* 1888 179 257 Low *Ber* 1890 23 3018

¹¹ Roth *German Patent Ber* 1890 23 (Referate) 714

¹² Benker *Chem Zeit* 1892 654 compare Groendahl and Lundin *Mon Scient* 1893 [4], 7, 11, 257

SECTION 7

ON THE METALS

The metals at present known, amount at least to 30 in number, they form a class of bodies which are remarkably distinguishable from others in several particulars, as well as from each other

Gravity One of the most striking properties of metals is their great weight or specific gravity. The lightest of them (excluding the lately discovered metals, potassium and sodium) weighs at least six times as much as water, and the heaviest of them 23 times as much. On the supposition that all aggregates are constituted of solid particles or atoms, each surrounded by an atmosphere of heat, it is a curious and important enquiry, whether this superior specific gravity of the metals is occasioned by the greater specific gravity of their individual solid particles, or from the greater number of them aggregated into a given volume, owing to some peculiar relation they may have to heat, or their superior attraction for each other. Upon examination of the facts exhibited by the metals, in their combinations

The density of ammonium nitrate is 1 709¹ 1 6973² at 23° C., 1 725³ at 15° C., and 1 725⁴ at 20° C. Its heat of formation from its elements is given as 87.9 Cal⁵ and 88.1 Cal⁶, and its specific heat as 0.407 between 0° and 31° C.⁷ Its solubility in water is given in the table⁸

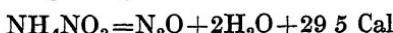
SOLUBILITY OF AMMONIUM NITRATE

Temperature, °C	Density of Solution.	Grams of NH_4NO_3 in 100 grams of Water	Solid Phase.
0		118.3	NH_4NO_3 rhombic β
12.2	1.2945	153.4	" " "
20.2	1.3116	192.4	" " "
30.0	1.3299	241.8	" " "
32.1	1.3344	256.9	" " " $\alpha + \beta$
35.0	1.3394	265.8	" " " α
40	1.3464	297.0	" " "
50		344	" " "
60		421	" " "
80		580	" " "
100		871	" rhombohedral ?

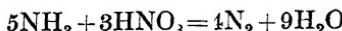
When heated, ammonium nitrate first melts, then dissociates in accordance with the scheme⁹



and commences to evolve a gas containing 98 per cent of nitrous oxide,⁹ the reaction beginning at 185° C.¹⁰



This gas always contains free nitrogen, nearly 2 per cent being present up to 260° C., and considerably more at higher temperatures.⁹



Traces of nitrogen peroxide and of nitric oxide are always present, the proportion of each between 220° and 260° C. averaging 0.001 per cent. The evolution of gas increases with rise of temperature, and is steady up to 250° C. At higher temperatures it becomes spasmodic, and

¹ Schiff *Annalen* 1858 107 59 1859 111 80

² Schiff and Monsacchi *Zeitsch physikal Chem* 1896, 21, 277

³ Retgers *ibid* 1889 4 592

⁴ Haigh *J Amer Chem Soc* 1912 34 1137

⁵ Berthelot *Ann Chim Phys* 1880 [5] 20 200 *Compt rend* 1880 90 779 *Bull Soc chim*, 1880 [2] 33 509

⁶ Thomsen, *J prakt Chem* 1880 [2] 21 449

⁷ Bellati and Romanese *Ann Physik Beibl* 1887 11 520 *Alt Inst Len* 1886 [6]

⁸ 1395

⁸ Muller and Kaufmann *Zeitsch physikal Chem* 1903 42 497 taken from Seidell *Solubilities of Inorganic and Organic Substances* (Crosby Lockwood & Son 1911)

⁹ Saunders, *Trans Chem Soc* 1922 121 698

¹⁰ Pickering *Chem News*, 1878 38 267 Velez, *Trans Chem Soc*, 1883, 43 370 compare Berthelot, *Compt rend*, 1876 82 932

if this be great, the heat is partly expressed or squeezed out, but if little, it is retained, though the attraction of the particles for heat remains unaltered An atom of water may have the same attraction for heat that one of lead has, but the latter may have a stronger attraction of aggregation, by which a quantity of heat is expelled, and consequently less heat retained by any aggregate of the particles

Opacity and Lustre Metals are remarkably opaque, or destitute of that property which glass and some other bodies possess, of transmitting light When reduced to leaves as thin as possible, such as gold and silver leaf, they continue to obstruct the passage of light Though the metallic atoms, with their atmospheres of heat, are nearly the same size as the atoms of water and their atmospheres, yet it seems highly probable that the metallic atoms abstracted from their atmospheres, are much larger than those of water in like circumstances The former, I conceive, are large particles with highly condensed atmospheres, the latter, are small particles with more extensive atmospheres, because of their less powerful attraction for heat Hence, it may be supposed, the opacity of metals and their lustre are occasioned A great quantity of solid matter and a high condensation of heat, are

Ammonium hypophosphate, $\text{NH}_4\text{H}_2\text{PO}_2$.—Evaporation of the solution obtained by mixing solutions of barium hypophosphate and ammonium sulphate yields a residue from which alcohol extracts ammonium hypophosphate, hexagonal¹ laminae or rhombic² plates, melting at 100° C. When heated above its melting-point it is converted into spontaneously inflammable phosphine, ammonia, and water.

Ammonium phosphites—Excess of ammonia reacts with phosphorous acid to form secondary ammonium phosphate, $(\text{NH}_4)_2\text{HPO}_3$, evaporation of the solution over sulphuric acid yielding the salt in four-sided

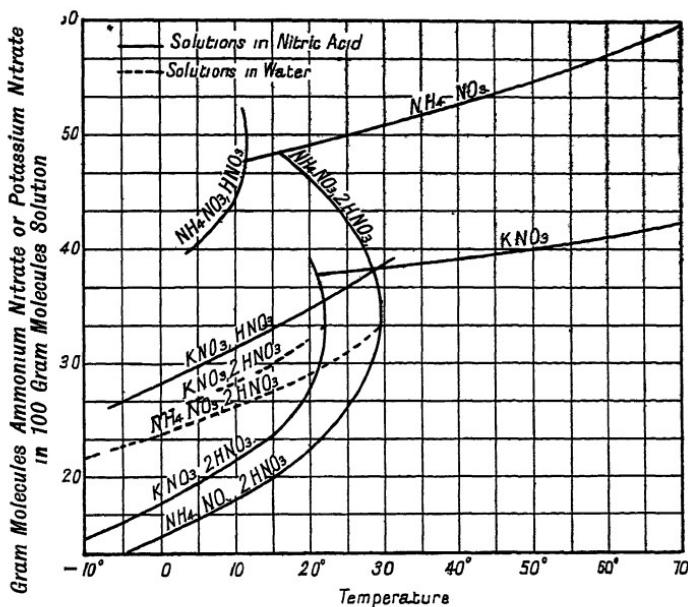


FIG. 12.—Solubility of ammonium nitrate, of potassium nitrate, and of their acid salts in nitric acid and of the trinitrates in water

columnar crystals of very deliquescent character³. It is also produced by the action of ammonia on the primary salt at 80° to 100° C,⁴ or on phosphorous oxide in presence of water. It readily loses ammonia and water, and strong heating produces phosphine and phosphoric acid³.

Primary ammonium phosphate, $\text{NH}_4\text{H}_2\text{PO}_3$, can be prepared from phosphorous acid by addition of sufficient ammonia to change the colour of methyl orange⁴. On concentrating the solution it separates in monoclinic prisms, melting at about 123° C. At 145° C it evolves ammonia, and at higher temperatures phosphine. Its solubility at 145° C is 190 grams in 100 grams of water⁴. At 100° C it is decomposed by water, with liberation of ammonia⁵.

Ammonium hypophosphates—Excess of ammonia converts hypophosphoric acid in solution into *normal ammonium hypophosphate*,

¹ Wurtz *Ann Chim Phys* 1843 [3] 7 193

² Beckenkamp *Zeitsch Kryst Min* 1903 37 618

³ Rose, *Pogg Annalen* 1828 12 85

⁴ Amat *Compt rend*, 1887, 105 809

⁵ Dufet *Bull Soc franq Min*, 1892 14, 206

Metals combine with various portions of oxygen, and form metallic *oxides*, they also combine with sulphur, and form *sulphurets*, some of them with phosphorus, and form *phosphurets*, with *carbone* or charcoal, and form *carburets*, &c which will be treated of in their respective places Metals also form compounds one with another, called *alloys*

The relative weights of the ultimate particles of the metals may be investigated, as will be shewn, from the metallic oxides, from the metallic sulphurets, or from the metallic salts, indeed, if the proportions of the several compounds can be accurately ascertained, I have no doubt they will all agree in assigning the same relative weight to the elementary particle of the same metal In the present state of our knowledge, the results approximate to each other remarkably well, especially where the different compounds have been examined with care, and can be depended upon, but the proportions of the elements in some of the metallic oxides, sulphurets, and salts, have not yet been found with any degree of precision

The number of metals hitherto discovered is 30, including the two derived from the fixed alkalis, some of these may, perhaps, be improperly denominated metals, as they are scarce, and have not been subjected to so much

to the monoclinic system,¹ with a saline, ammoniacal taste, and density 1.554.² It loses ammonia readily, and is converted by heat into secondary sodium phosphate. When heated with metallic salts it forms vitreous "microcosmic beads" of characteristic colour, and is employed in qualitative analysis.

Potassium diammonium phosphate, $K(NH_4)_2PO_4 \cdot 4H_2O$, is obtained by passing ammonia into a cooled solution of potassium dihydrogen phosphate, and filtering rapidly in an atmosphere of ammonia. On exposure to air, the deliquescent salt evolves ammonia, but it can be preserved in sealed tubes.³ Other double salts with sodium,⁴ and with lithium⁵ and potassium,⁶ have been prepared.

Ammonium pyrophosphates—Excess of ammonia reacts with pyrophosphoric acid to form *normal ammonium pyrophosphate*, $(NH_4)_2P_2O_7$, precipitated from aqueous solution by addition of alcohol. It forms crystalline laminae, dissolving very readily in water to a solution of alkaline reaction.⁷ When boiled, this solution evolves ammonia, yielding an acid solution of *secondary ammonium pyrophosphate*, $(NH_4)_2H_2P_2O_7$.

Double pyrophosphates with sodium⁸ and with potassium⁹ have also been described.

Ammonium metaphosphates—Several metaphosphates are known,¹⁰ among them *ammonium monometaphosphate*, NH_4PO_3 , formed from the dimetaphosphate by prolonged heating at 200° C.¹¹ It is only slightly soluble in water.

Ammonium arsenites—Between 70° and 80° C ammonia reacts with a solution of arsenious oxide to form acicular crystals of *ammonium meta-arsenite*, NH_4AsO_2 .¹² With concentrated ammonia arsenious oxide yields the crystalline *ammonium pyroarsenite*, $(NH_4)_4As_2O_5$, an unstable substance decomposed with evolution of ammonia on exposure to air.¹³

Ammonium arsenates—Excess of ammonia precipitates *normal ammonium arsenate*, $(NH_4)_3AsO_4$, from concentrated solutions of the primary and secondary salts. It yields a very alkaline solution, decomposed by zinc and by aluminium with evolution of hydrogen and arsine.¹⁴ *Secondary ammonium arsenate*, $(NH_4)_2HAsO_4$, is gradually deposited from a concentrated solution of arsenic acid and ammonium hydroxide.¹⁵ Loss of ammonia, or addition of arsenic acid to its solution, converts it into *primary ammonium arsenate*, $NH_4H_2AsO_4$, crystals of density 2.307¹⁶ or 2.3105.¹⁷

¹ Thomson and Bloxam *Trans Chem Soc* 1882 41 379

² Schiff *Annalen* 1859, 112 88

³ Corelli *Gazzetta* 1921 51 11 380

⁴ Uelmann *Arch Pharm* 1859 [2] 99 138 Herzfeld and Feuerlein *Zeitsch anal Chem* 1881 20 191 Meslin *Compt rend* 1905 140 782

⁵ Berzelius *Lehrbuch der Chemie*, 3rd ed Dresden 1833-1841, 4 213

⁶ Filhol and Senderens *Compt rend* 1882 94 649

⁷ Schwarzenberg *Annalen* 1848 65 141

⁸ Schwarzenberg *loc cit* Rammelsberg *Ann Physiol* 1883 [2] 20 943

⁹ Schwarzenberg *loc cit* Retgers *Zeitsch physikal Chem* 1894 15 529

¹⁰ Compare metaphosphoric acid this series Vol VI

¹¹ Kleitmann *Pogg Annalen* 1849 78 233 238

¹² Luynes *J prakt Chem* 1857 72 80

¹³ Pasteur *Annalen* 1848 68, 308 Stein *ibid* 1850 74, 218

¹⁴ Smith *J Soc Chem Ind*, 1904 23 475 1911 30 253

¹⁵ Salkowsky *J prakt Chem*, 1868 104, 129

¹⁶ Schroder, *ibid*, 1879 [2] 19 266

¹⁷ Muthmann, *Zeitsch Kryst Min*, 1894, 22, 497

4 Refractory

1 Titanium 3 Tantalum

2 Columbium 4 Cerium

To which last class also may the supposed metals from the earths be referred

The following Table exhibits the chief properties of the metals in an absolute as well as comparative point of view

Metals	Colour	Hardness	Sp Gr	Wt of ult particles	Melting point	Tenacity
Gold	yellow	6	19 362	140?	32° W	150
Platin	white	7 5	23 00	100?	170° +W	274
Silver	white	6 5	10 511	100	22° W	187
Merc	white	0	13 580	167	—39° F	—
Pallad	white	9	11 871	—	160° +W	—
Rhod	white	—	11 +	—	160° +W	—
Irid	white	—	—	—	160° +W	—
Osm	blue	—	—	—	160° +W	—
Copper	red	8	8 878	56	27° W	302
Iron	grey	9	7 788	50	159° W	550
Nickel	white	8	8 666	2,? 50?	160° +W	—
Tin	white	6	7 300	50	410° F	31
Lead	blue	5	11 352	95	612° F	18
Zinc	white	6	7 190	50	680° I	18
Potas	white	0	600	15	80° I	—
Sodium	white	1	9 35	21	150° F	—
Bism	red wh	6	9 823	64?	476° F	20
Antim	grey w	6 5	6 860	40	510° I	7
Tellur	blue w	—	6 343	—	612° +I	—
Arsenic	blue w	7	8 31	42?	400° +I	—
Cobalt	grey	8	7 811	55?	130° W	—
Mang	grey	8	7 000	40?	160° W	—
Chrom	yel w	—	—	—	170° +W	—
Uran	iron gi	—	9 000	60?	170° +W	—
Molyb	yel w	—	7 500	—	170° +W	—
Lungs	grey w	9	17 6	56?	170° +W	—
Titan	red	—	—	40?	170° +W	—
Colum	—	—	—	—	170° +W	—
Tantal	—	—	—	—	170° +W	—
Cerium	white	—	—	45?	170° +W	—

1 573¹ and 1 544² at 15° C. Its solubility at 17 1° C. is 19.35 grams in 100 grams of water,³ the salt crystallizing well from aqueous solution. It is a product of the decomposition of the normal carbonate at ordinary temperature.⁴

A *tetra-ammonium dihydrogen carbonate*, $(\text{NH}_4)_4\text{H}_2(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$, can be prepared by heating the commercial salt to fusion, and allowing the liquid to solidify⁴, by crystallizing the commercial salt from warm ammonium hydroxide⁵; and by the action of alcohol on the normal salt⁶. It forms rhombic plates and prisms, soluble in 5 times their weight of water at 15° C. Its properties are intermediate between those of the normal carbonate and the primary carbonate, and it is doubtful whether it is a definite compound or a mixture of these two salts.

Commercial ammonium carbonate is a mixture of ammonium hydrogen carbonate and *ammonium carbamate*, $\text{NH}_2\text{COONH}_4$, and is probably a definite compound of the two salts⁷. It is formed by distillation of a mixture of ammonium chloride with carbonate of potassium, sodium, or calcium, and was formerly manufactured by the dry distillation of animal excrement, horn, and other substances. It is now obtained as a by-product of the gas-manufacture, and after sublimation condenses in hard lumps.

Ammonium cyanide, NH_4CN —The cyanide is manufactured by passing ammonia alone or mixed with hydrocarbons⁸ over red-hot coke, or by heating ammonia with carbon monoxide



or by passing a mixture of ammonia, hydrogen, and nitrogen over coke at 1100° C.⁹ It is also a by-product in the manufacture of coal-gas,¹⁰ and is formed by the interaction of ammonia and calcium carbide at 650° C.¹¹ Other methods of formation are the combination of methane and nitrogen under the influence of the silent electric discharge,¹² and the distillation of ammonium chloride with anhydrous cyanides.¹³

Ammonium cyanide forms colourless cubes, readily volatilized and completely dissociated at comparatively low temperatures.¹⁴ Its heat of formation from diamond, hydrogen, and nitrogen is 3.2 Cal.¹⁵ It dissolves readily in both water and alcohol, the salt being extensively dissociated in aqueous solution. It is extremely poisonous.

Ammonium thiocyanate, NH_4CNS —The thiocyanate is manu-

¹ Schiff *Annalen*, 1858, 107, 64.

² Dibbits *J. prakt. Chem.* 1874, [2] 10, 434.

³ Divers *J. Chem. Soc.* 1870, 23, 171, 359, 364. Deville *Ann. Chim. Phys.* 1854,

[3] 40, 87. *J. prakt. Chem.* 1854, 62, 22. Vogler *Zeitsch. anal. Chem.* 1878, 17, 451.

⁴ Rose *Pogg. Annalen* 1839, 46, 400.

⁵ Deville *loc. cit.*

⁶ Divers *loc. cit.*

⁷ Compare Dibbits *loc. cit.*

⁸ Ianglois *Berzelius's Jahresbericht* 1822, 84. compare Bergmann *J. Gasbeleuchtung* 1896, 39, 117, 140.

⁹ Lincee *Compt. rend.* 1897, 124, 819.

¹⁰ Pendié *J. Gasbeleuchtung* 1888, 31, 1006.

¹¹ Salvadori *Gazzetta* 1905, 35, 1, 236.

¹² Figuer *Compt. rend.* 1886, 102, 694.

¹³ Bineau *Annalen* 1839, 32, 230.

¹⁴ Bineau *loc. cit.* Ostwald *Lehrbuch der allgemeinen Chemie* 1st ed. Leipzig 1880–1887, 2, 687. Deville and Troost *Compt. rend.* 1859, 49, 239. 1863, 56, 891. *Annalen* 1860, 113, 42, 1863, 127, 274.

¹⁵ Berthelot, *Compt. rend.*, 1880, 91, 79.

ing reduced to $\frac{1}{12}$ th of that thickness on silver wire Gold melts at 32° of Wedgwood's pyrometer , that is, a red heat, but one greatly inferior to what may be obtained by a smith's forge when fused, it may continue in that state for several weeks without losing any material weight There is reason to believe that gold combines with oxygen, sulphur, and phosphorus , but those compounds are difficultly obtained It combines with most of the metals, and forms alloys of various descriptions

The weight of an atom of gold is not easily ascertained, because of the uncertainty in the proportions of the elements forming the compounds into which it enters It is probably not less than 140, nor more than 200 times the weight of an atom of hydrogen

PLATINA This metal has not been found any where but in South America In its crude state, it consists of small flattened grains of a metallic lustre, and a grey-white colour This ore is found to be an alloy of several metals, of which platina is usually the most abundant The grains are dissolved in nitro-muriatic acid, except a black matter which subsides , the clear liquor is decanted, and a solution of sal ammoniac is dropped into it a yellow precipitate falls , this is heated to redness, and the

crystals¹ of the *pentaborate*, $(\text{NH}_4)_2\text{O}, 5\text{B}_2\text{O}_3, 8\text{H}_2\text{O}$, soluble in 8 times their weight of cold water

The mineral *larderellite*, $(\text{NH}_4)_2\text{O}, 4\text{B}_2\text{O}_3, 5\text{H}_2\text{O}$, is found in nature in association with boric acid in the lagoons of Tuscany.

Ammono-salts of the Alkali-metals—The interaction of metallic amides in ammonia solution produces the so-called *ammono-salts*²

Dipotassium ammonosodiate, $(\text{Na}[\text{NH}_2]_3)\text{K}_2$, is formed by the action of potassamide on sodamide in solution in liquid ammonia, by bringing sodium iodide into contact with excess of potassamide dissolved in liquid ammonia, and by the interaction in presence of a small proportion of platinum-black of sodium and a solution of potassamide in liquid ammonia. This substance forms well-developed crystals, and is stable *in vacuo* at 100° C , but at higher temperatures it melts with evolution of ammonia, and attacks glass

Monorubidium ammonosodiate, $(\text{Na}[\text{NH}_2]_2)\text{Rb}$, is the product of the simultaneous action of sodium and rubidium on liquid ammonia. It is soluble in this solvent, and is energetically decomposed by water with formation of sodium and rubidium hydroxides. Its solution in liquid ammonia is converted by a large excess of rubidium into *dirubidium ammonosodiate*, $(\text{Na}[\text{NH}_2]_3)\text{Rb}_2$, a substance much more soluble in liquid ammonia than its parent compound

Dipotassium ammonolithrate, $(\text{Li}[\text{NH}_2]_3)\text{K}_2$, is formed from potassamide and lithium iodide in solution in liquid ammonia, and under the influence of platinum-black by the simultaneous action of potassium and lithium on liquid ammonia. The very small, colourless crystals are almost insoluble in liquid ammonia. With acid amides, ammonium halides, and ammonium salts of oxy-acids it yields the corresponding salts of lithium, potassium, and ammonium

Monorubidium ammonolithuate, $(\text{Li}[\text{NH}_2]_2)\text{Rb}$, is prepared by the action in presence of platinum-black of lithium on rubidamide dissolved in liquid ammonia. The white crystals are sparingly soluble in liquid ammonia, and are decomposed analogously to those of the dipotassium derivative

¹ Atterberg *Zeitsch anorg Chem* 1906 **48** 371
Franklin, *J Physical Chem* 1919, **23**, 36

oxygen, it should seem to be about 100, but, judging from its great specific gravity, one would be inclined to think it must be more. Indeed the proportion of oxygen in the oxides of platina cannot be considered as ascertained.

Platina is chiefly used for chemical purposes, in consequence of its infusibility, and the difficulty of oxidizing it, crucibles and other utensils are made of it, in preference to every other metal. Platina wires are extremely useful in electric and galvanic researches, for like reasons.

SILVER This metal is found in various parts of the world, and in various combinations, but the greatest quantity is derived from America. Its uses are generally known. The specific gravity of melted silver is 10 474, after being hammered, 10 511. English standard silver, containing $\frac{1}{2}$ copper, simply fused, is 10 2. Pure silver is extremely malleable and ductile, but inferior in these respects to gold. It melts at a moderately red heat. It is not oxidized by exposure to the air, but is tarnished or loses its lustre, which is occasioned by the sulphureous vapours floating in the air. It unites with sulphur in a moderate heat, and may be oxidized by means of galvanism and electricity, it burns with a green flame.

vases of Cyprian origin dating from the same period have been found in Egypt. The metal employed in their manufacture was free from tin. The great metallurgical skill possessed by the makers of these vessels proves that copper must have been known in Cyprus for many centuries previous to their production.

Copper daggers found in Northern Italy probably date from about the year 2100 B.C.¹. Keith² gives the date 2000 B.C. for the beginning of the Bronze Age in Britain, five centuries later than the date suggested by Montelius³. Copper was probably known in China about the year 3000 B.C. There is evidence of its having been worked in India at an early period.

The association of the ores of copper with those of other metals is probably the cause of the production of alloys of varying composition by the prehistoric smelters. The earliest copper tools of Britain contain tin, those of Hungary up to 45 per cent of antimony⁴.

Chinese and Japanese bronze mirrors dating from the first, fifth, seventh, eleventh, and twelfth centuries have been found to contain between 62 and 74 per cent of copper associated with other metals. A Corean mirror of the tenth century contains 73 per cent of copper, and considerable proportions have been found in ancient coins, arrow-heads, and water-pots from these lands⁵.

Copper deposits in Britain are said to have been known to the Phoenicians about the year 1000 B.C. In 1581 mining was being carried on at Keswick, in Cumberland, the ore being probably a sulphide. The Mines Royal Society established a works for copper-smelting at Neath, in Wales, in 1584. Various other works were started in Wales at different times, notably those erected by Lane and Pollard at Swansea in 1717.

The production of copper in Cornwall and Devon continued from the time of Queen Elizabeth to the end of the nineteenth century. In Ireland the industry was carried on from the beginning of the eighteenth century until 1880. The copper of Anglesey was known to the Romans, and the mines of the island were worked during the eighteenth and nineteenth centuries.

Reverberatory furnaces were constructed by Lambert in Chile in 1842, and the first blast furnace was erected by him in that country in 1857. So successful was the development of this enterprise, that Chile became the world's largest producer in the years 1861 to 1870, and furnished about half the total output. The decline of the Welsh industry dates from this period, and also the development of the manufacture in the United States of America, Calumet, in the Lake Superior district, becoming an important centre. The next decade is noted for the inception of copper-mining in Spain and Portugal, the chief centres being the Andalusian, San Domingo, Tharsis, and Rio Tinto mines.

Between 1881 and 1890 the United States of America became the greatest producer, manufacturing one third of the world's output. In addition to the Lake mines, works were begun in Montana and Arizona.

¹ Montelius, *J. Anthropol. Inst.* 1897, 26 258.

² Keith, Presidential Address to the Royal Anthropological Institute January 26 1915.

³ Montelius *Archeologia* 1909, 61 162.

⁴ Compare Berthelot *Compt. rend.* 1893 116 161 1894 118 764 1897 124 328.

Ann. Chim. Phys. 1889 [6] 17 508, Coffey *J. Anthropol. Inst.* 1901 31 265.

⁵ Chikashige, *Trans. Chem. Soc.*, 1920 117 917.

smell, it may be taken internally, without producing any remarkable effect on the human body It can be united with oxygen, sulphur, and phosphorus, and it forms alloys, or, as they are more commonly called, *amalgams*, with most of the metals

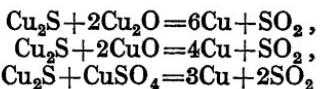
The weight of an atom of mercury is determinable from its oxides, its sulphuret, and the various salts which it forms with acids from a comparison of all which, it seems to be about 167 times the weight of hydrogen From any thing certainly known, the mercurial atom is heavier than any other, though there are two or three metals which exceed it in specific gravity

PALLADIUM This metal was discovered a few years ago in crude platina, by Dr Wollaston, of which an account may be seen in the Philos Transact for 1804 It is a white metal, resembling platina in appearance, but is much harder it is only one half of the specific gravity of platina It requires great heat to fuse it, and is difficultly oxidized Palladium combines with oxygen and sulphur, and forms alloys with several of the metals But we have not yet sufficient data to determine the weight of its ultimate particles

RHODIUM This metal has been discovered still more recently than the last in crude pla-

The German or Swedish process involves five steps. (1) roasting the ore, (2) smelting the roasted ore to *matte* in a blast furnace; (3) roasting the matte, (4) smelting the matte in a blast furnace with coke and fluxes to *black-metal* or *coarse-metal*; (5) refining the coarse-metal. During the process the siliceous material and part of the iron are converted into a fused silicate-slag, floating on a heavier layer of copper matte consisting of a fused mixture of cuprous sulphide and ferrous sulphide. The reduction to copper is effected chiefly by carbon monoxide or carbon, and not by the sulphur present. To concentrate the matte, the cycle of oxidation by roasting and reduction by smelting is repeated several times, the iron being gradually removed as a fused slag of ferrous silicate.

The English process comprises six operations. (1) calcination, (2) smelting to *matte* in a reverberatory furnace, (3) roasting the matte; (4) smelting the matte in a reverberatory furnace to *white-metal* or *fine-metal*, (5) conversion of the fine-metal into *coarse-copper* or *blister-copper*, sometimes after a preliminary calcination, (6) refining the coarse-copper. In this process the calcined ore is smelted in a reverberatory furnace, the reduction being effected by the interaction of the sulphides and oxides or sulphates, with evolution of sulphur dioxide, thus yielding a more concentrated matte than the blast-furnace process.



The siliceous lining of the hearth converts the ferrous oxide into a slag of ferrous silicate. By altering the air-supply to the furnace, the matte is subjected to alternate oxidation and reduction. Both the German process and the English process depend on the fact that copper has a greater affinity for sulphur than for oxygen, and iron a greater affinity for oxygen than for sulphur.

The Welsh process differs from the English method in the enrichment of the matte by smelting with copper slags formed in subsequent operations.

The Anglo German process is a combination of the English and German methods. After calcination the ore is smelted in a shaft furnace, and the matte is concentrated in a reverberatory furnace. The subsequent smelting to coarse metal can be effected in either type of furnace.

The concentration of the matte and its subsequent smelting to coarse-copper are also effected by the Bessemer process, a modified type of Bessemer converter with the side tuyeres raised about 10 inches above the bottom lining being employed. The process finds extensive application, a large proportion of the arsenic and antimony being eliminated. A serious item of expense is the renewal of the siliceous lining of the converter, the silica required for slagging the iron being provided from this source.

In localities where fuel is expensive, *pyritic smelting*¹ has been considerably developed. It was devised by John Holway² in 1878.

¹ Schiffner Rep 5th Internat Congress Appl Chem, 1903 p 102, London ibid 251

² Holway A New Application of Bessemer's Method of Rapid Oxidation by which Sulphides are utilized as Fuel, Royal Society of Arts, February 1879

weights of the atoms of these two metals are unknown

COPPER This metal has been long known It is of a fine red colour, its taste is styptic and nauseous Its specific gravity varies from 8.6 to 8.9 It possesses great ductility, can be drawn into wire as fine as hair, and is capable of being beaten into very thin leaves It is fused in a temperature higher than silver, and lower than gold, about 27° of Wedgwood's thermometer Copper unites with oxygen, sulphur, and phosphorus, and forms alloys with several other metals

The weight of the ultimate particle of copper, may be ascertained with considerable precision, from the proportions in which it is found combined with oxygen, sulphur, and phosphorus, as well as from its combinations with the acids From a comparison of these, its weight seems to be nearly 56 times that of hydrogen

IRON This metal, the most useful we are acquainted with, has been long known It seems to be found almost in every country, and in a great variety of combinations Its ores require great heat to expel the foreign matters, and to melt the iron, which is first obtained in masses or pigs, called *cast iron*,

poling is deleterious, causing the reduction of arsenates and antimonates to the corresponding elements, and thus deteriorating the quality of the copper. The soft, malleable metal is known as *tough-pitch* copper, and displays a lustrous, silky fracture. Several varieties of copper are recognized in the trade: *bean-shot* copper is formed by pouring the metal into hot water; *feathered-shot* copper by pouring into cold water; *rosette* copper by cooling the surface of the fused metal with water, and removing the thin, dark red crust formed; *japan* copper by casting into ingots, and cooling rapidly with water, its colour being purple-red; *file* copper, an impure form produced by refining the first tappings; *best-selected* copper, a purer type.

(2) WET METHODS

Wet methods of extraction are applied to low-grade ores containing not less than 0.25 to 1 per cent of copper, or to products containing copper associated with gold and silver. For ores containing copper as oxide or carbonate, the solvents employed are sulphuric acid, hydrochloric acid, and ferrous chloride.

The original Hunt-Douglas process¹ involves treatment of the ore at 70° C with a solution of ferrous chloride produced by the interaction of sodium chloride and ferrous sulphate. The ferrous chloride converts copper oxide and carbonate into a solution of cuprous and cupric chlorides, ferric hydroxide being precipitated and carbon dioxide evolved. After filtration to remove ferric hydroxide the copper is precipitated by addition of scrap iron, the ferrous chloride thus regenerated being available for further use in the first stage of the process. The amount of iron required is small, but the method is handicapped by difficulty in filtering the ferric hydroxide, by the tendency of the copper solution to undergo atmospheric oxidation, and by the fact that any silver present is dissolved.

In the modern Hunt-Douglas process the ore is leached with dilute sulphuric acid, and the copper converted into cupric chloride by addition of ferrous chloride or calcium chloride. The use of the calcium salt entails removal of the calcium sulphate by filtration. The cupric salt is precipitated as cuprous chloride by reduction with sulphur dioxide, and the precipitate is converted into metallic copper by treatment with iron, or into cuprous oxide by the action of milk of lime. In this process the amount of iron needed is proportionately small, ferric hydroxide is not precipitated, and silver is not dissolved.

When the ore contains cuprous sulphide this salt is converted into a soluble form—cupric sulphate, soluble in water; cupric oxide, soluble in hydrochloric or sulphuric acid; cupric chloride, soluble in water; or cuprous chloride, soluble in solutions of metallic chlorides.

Conversion into the sulphate is effected by weathering, a slow and expensive process, by calcination, for ores containing a high percentage of iron pyrites, by calcination with ferrous or aluminium sulphate, or by calcination with ferric sulphate as an adjunct to the weathering process.

The transformation into oxide is carried out by calcination in a reverberatory furnace, or, if the sulphur is to be recovered, in a muffle

¹ Hunt *Compt rend.*, 1869, 69 1357 A Meyer *Berg und Hüttenmannsche Zeit* 1862 21, 182

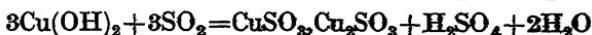
any of the salts which it forms with acids all these will be found to give the same weight nearly, namely, 50 times the weight of an atom of hydrogen

NICKEL The ore from which this metal is obtained, is found in Germany it usually contains several other metals, from which it is difficult to extract the nickel in a state of tolerable purity Nickel, when pure as it can be obtained, is of a silver white colour, its specific gravity is 8 279, and when forged 8 666 It is malleable, both hot and cold, and may be beaten into a leaf of $\frac{1}{100}$ of an inch in thickness A very great heat is required to fuse it It is attracted by the magnet nearly as much as iron, and may be converted into a magnet itself It combines with oxygen, sulphur, and phosphorus, and may be alloyed with certain other metals

The weight of its atom can scarcely yet be determined, for want of a more accurate knowledge of the compounds into which it enters perhaps it will be found to weigh about 25, or else double that number, 50

TIN This metal has been long known, though it is found but in few places comparatively Cornwall is the only part of Great Britain where this metal abounds, and its tin mines are the most celebrated in Europe Tin

The process patented by Jumau¹ involves the extraction of the roasted ore with an ammoniacal solution of ammonium sulphate or sulphite. Sulphurous acid reacts with the solution thus formed, precipitating either cuprous sulphite or cupro-cupric sulphite.



The precipitated sulphite is redissolved in an ammoniacal solution of ammonium sulphate or sulphite, and the solution electrolyzed.

Electrolytic Refining.²—In 1865 Elkington patented a process for the electrolytic refining of copper, similar in principle to the method employed at the present day. In the modern process the bath is a solution containing 12 to 20 per cent of copper sulphate and 4 to 10 per cent. of sulphuric acid. A fairly pure anode of copper containing small amounts of silver, gold, arsenic, antimony, iron, and other impurities is employed, the metal being deposited on a copper cathode. A pure and coherent deposit of copper is obtained with a low current-density of 0.0043 to 0.0484 ampere per sq cm., the noble metals being deposited in the anode mud, and the other impurities remaining partly in this mud, and partly entering into solution. If the current-density be too low, the deposited copper is pale and brittle, if too high, it is dark-brown and spongy. Constant attention must be paid to the composition and degree of acidity of the electrolyte, both important factors influencing the nature of the deposit. With rotating cathodes a good deposit is obtained with currents of high density, but in practice this modification is precluded by the disturbance of the anode mud, the solid particles in the electrolyte causing the formation of nodular growths on the deposited copper. The yield of copper obtained by the electrolytic method usually corresponds with a current efficiency of 94 to 96 per cent, although it is possible to attain an efficiency of 98 per cent. The bath is usually maintained at a temperature of 40° to 50° C.

Jumau's process (*ut supra*) for the electrolytic extraction of copper from its ores is also applicable to the production of pure copper from solutions of its compounds³. The cupric sulphite or cupro-cupric sulphite precipitated from the copper solution by the action of sulphurous acid or a sulphide is decomposed by sulphuric acid into cupric sulphate and metallic copper. The metal thus liberated is pressed into a form suitable for an anode, and refined electrolytically.

Refining by other Methods—Various other methods are available for the purification of copper. An example is the ready reduction of cuprous chloride by soft iron, a substance without action on cupric chloride. Aluminium slowly reduces a warm solution of cupric sulphate. Vigorous⁴ recommends a method depending on the action of aluminium on a solution of copper in concentrated hydrochloric acid.

¹ German Patents 1907 Nos 189643 and 191566.

Compare Ulke *Elektrolytische Raffination des Kupfers* Halle 1904 Borchers *Elektrometallurgie* 3rd ed Leipzig 1903, 185 Haber *Zeitsch Elektrochem.*, 1903 9, 384, Addicks, *Trans Amer Electrochem Soc.*, 1904 5 120 Forster and Seidel *Zeitsch anorg Chem.*, 1897, 14, 106 Forster and Coffetti *Ber.*, 1905 38 2934 Ullmann *Zeitsch Elektrochem.*, 1897 3, 516, Sand, *Zeitsch physikal Chem.* 1901 35 641 Schwab and Baum *J Physical Chem.*, 1903, 7 614 *Trans Amer Electrochem Soc.* 1903 4 55 von Hübner, *Mittheil militär geograph Inst.*, 1888 6 51 Swan, *J Soc Chem Ind.* 1901, 20 663 Kilian *Berg und Hütten mannische Zeit.*, 1885, 44, 249 McJohnson *Trans Amer Electrochem Soc.*, 1901, 2, 171.

² German Patent 1907 No 189974 1908, No 204673.

⁴ Vigorous, *Bull Soc chim.*, 1907, [4], 1, 7.

phosphorus, and forms alloys with most other metals

The ultimate particle of lead, as deduced from a comparison of its oxides, sulphuret, and the salts in which it is found, I estimate at 95 times that of hydrogen

ZINC The ores of this metal are not rare, but the metal has not been extracted from them in a pure state, at least in Britain, much more than half a century Zinc is a brilliant white metal, inclining to blue. Its specific gravity is from 6.9 to 7.2 It was till lately considered as a brittle metal, but Messrs Hobson and Sylvester, of Sheffield, have discovered that between the temperature of 210° and 300°, zinc yields to the hammer, may be laminated, wire drawn, &c and that after being thus wrought, it continues soft and flexible It melts about 680°, and above that temperature evaporates considerably Zinc soon loses its lustre in the air, and grows grey, but in water it becomes black, and hydrogen gas is emitted Zinc combines with oxygen, and either it or its oxides combine with sulphur and phosphorus It forms alloys with most of the metals, some of which are very useful

The atom of zinc weighs nearly 56 times as much as hydrogen

POTASSIUM We are principally indebted to

copper is almost as great as that of silver,¹ the ratio at 18° C being 100 : 96.4 It has been suggested that copper can dissolve to a minute extent in water.²

The possibility of the existence of a metastable form of copper has been discussed by Cohen and Inouye.³

The molecular weight of the vapour has not been determined, but in solution in mercury,⁴ molten tin,⁵ and molten lead⁶ the molecule is monatomic

Occlusion of Gases

Solid copper occludes hydrogen (p. 23), but not nitrogen, carbon monoxide, or sulphur dioxide.⁷ Merton⁸ found that precipitated copper readily absorbs gases, which are expelled at high temperature. After a few weeks its power of absorption vanishes.

Molten copper absorbs hydrogen⁹ and sulphur dioxide,¹⁰ the occluded gases being eliminated on cooling. The liquid metal does not absorb nitrogen. It combines with oxygen to form cuprous oxide, so that fall of temperature is not attended by evolution of the gas. It decomposes hydrocarbons such as methane and ethane, with occlusion of hydrogen and separation of carbon.

According to Stahl,¹¹ the absorption of gases by molten copper generally becomes greater with the temperature up to a certain point, with increase in the purity of the metal, and with the partial pressure of the gas. At 650° C 100 grams of copper dissolve 0.1 milligram of hydrogen, and at 1500° C 1.4 milligram, the solubility of the gas in both solid and liquid copper increasing as the square root of the pressure. The absorbed hydrogen has no influence on the conductivity of the metal. At 1420° C 61 grams of copper absorb 0.15 c.c. of carbon monoxide, the physical properties of the metal undergoing a marked change.

At 800° C and higher temperatures the ductility of copper is considerably increased by the presence of oxygen, but above 720° C hydrogen has a weakening effect.¹²

Electrolysis of a neutral or slightly alkaline solution of cupric acetate with a copper anode and a platinum cathode yields a deposit regarded by Schutzenberger¹³ as an allotropic form of copper. It is a very brittle, bronze-coloured substance of low specific gravity and high electric resistance. It readily undergoes atmospheric oxidation, and decomposes nitric acid with evolution of nitrous oxide. Schutzenberger's original product contained cuprous oxide, and Wiedemann¹⁴ attributed its properties to the presence of this substance. It is possible, however,

¹ Compare Niccolai *Atti R. Accad. Lincei* 1907 [5] 16 1 906

Traube, Mangarini and Scala *ibid* 1909 [5] 18 1 542

² Cohen and Inouye *Chem. Weekblad* 1909 6 881

³ G. Meyer *Zeitsch. physikal. Chem.* 1891 7 477

Heycock and Neville *Trans. Chem. Soc.* 1890 57 376

⁴ Heycock and Neville, *ibid.* 1892 61 888

⁵ Sieverts *Zeitsch. Elektrochem.* 1910 16 707 Sieverts and Krumbhaar *Zeitsch. physikal. Chem.* 1910 74, 277 Stubbs *Trans. Chem. Soc.* 1913 103 1440

⁶ Merton *Trans. Chem. Soc.*, 1914 105 645

⁷ Sieverts *Zeitsch. physikal. Chem.* 1907 60 129

⁸ Sieverts *Zeitsch. Elektrochem.* 1910 16 707 Sieverts and Krumbhaar *loc. cit.*

⁹ Stahl *Metall und Erz* 1914 11 470

¹⁰ Bengough and Hanson *J. Inst. Metals* 1914 12 56

¹¹ Schutzenberger *Compt. rend.* 1878 86 1265

¹² Wiedemann, *Pogg. Annalen* 1879 [2] 6 81, compare Schutzenberger *Bull. Soc. chim.*, 1879, [2] 31 291

left to future experience — Potassium, at the temperature of 32°, is solid and brittle, and its fragments exhibit a crystallized texture at 50°, it is soft and malleable, at 60°, it is imperfectly fluid, at 100°, it is perfectly fluid, and small globules unite as in mercury. It may be distilled by a heat approaching to redness. Its specific gravity is only 6, this circumstance would seem to countenance the notion of its containing hydrogen. Potassium combines with oxygen, sulphur, and phosphorus, and it seems to form alloys with many of the metals.

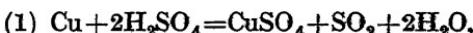
The weight of an atom of potassium appears from its combination with oxygen to be 35 times that of hydrogen.

SODIUM Mr Davy obtained this metal from the fixed mineral alkali, or soda, by means of galvanism, in the same way as potassium. Sodium, at the common temperature, is a solid, white metal, having the appearance of silver, it is exceedingly malleable, and much softer than other metallic substances. Its specific gravity is rather less than water, being 9348. It begins to melt at 120°, and is perfectly fluid at 180°. It combines with oxygen, sulphur, and phosphorus, and forms alloys with the metals.

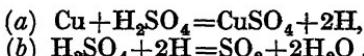
The weight of an atom of sodium, as de-

oxygen is absorbed slightly more rapidly than the moist gas. At ordinary pressure and temperature chlorine combines with the metal to form cupric chloride and a small proportion of the cuprous salt, at a high temperature cuprous chloride is the sole product. When copper is heated in gaseous hydrogen chloride, cuprous chloride is produced, and hydrogen evolved¹. At 1200° C the metal reacts slowly with carbon dioxide, forming cuprous oxide and carbon monoxide.² An arc between copper poles burns in carbon dioxide almost as well as in air, but very imperfectly in coal-gas or steam.³

Copper is not attacked by water at ordinary temperatures, or at 100° C, and only slightly at white heat, but very prolonged immersion in sea-water produces a superficial coating of cuprous oxide.⁴ It is insoluble in dilute sulphuric acid of 5 to 10 per cent strength,⁵ but reacts with the concentrated acid in accordance with the equations⁶



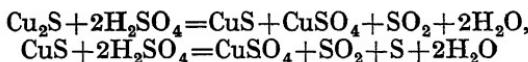
this reaction probably taking place in the two stages



and

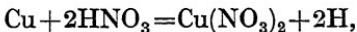


The first reaction proceeds between 0° and 270° C, the second accompanying it between 0° and 100° C. When the copper is exhausted, the cuprous sulphide is then decomposed in accordance with the equations

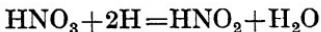


The black residue formed in the reaction appears to be mainly cuprous sulphide

Nitric acid dissolves copper, forming cupric nitrate and oxides of nitrogen. The primary process corresponds with the equation



but hydrogen is not evolved, being oxidized to water by the nitric acid. The action is conditioned by the presence of nitrous acid as a catalyst, since in absence of this acid the velocity of solution of copper in nitric acid of moderate concentration is very small. A similar retardation is produced by addition of substances capable of reacting with nitrous acid such as perchlorates, permanganates, hydrogen peroxide or urea. The velocity of the reaction



¹ Wohler *Annalen* 1858 105 360

² von Bacho *Monatsh* 1916 37 119

³ Hagenbach *Physikal Zeitsch* 1909, 10 649

⁴ Jorissen *Chem Weekblad* 1909 6 150

⁵ Gannon *Proc Roy Soc* 1893 55 66 Schuster *ibid* 84

⁶ Lunge *Chem Industrie* 1886 9, 47 Pickering *Trans Chem Soc* 1878 33 112 Baskerville *J Amer Chem Soc* 1895 17 904 1896 18 942 van Deventer *Chem Weekblad* 1905 2 137 1906, 3 515 Sluiter *ibid* 1906 3 63

⁷ Millon *Ann Chim Phys* 1842 [3] 6 95, *J prakt Chem* 1843 29 338 Veley *Chem News* 1889 59 303 1891 63 3, *Proc Roy Soc* 1890 48 458 Ihle *Zeitsch physikal Chem.*, 1895, 19 577

determinable from its compounds with oxygen and sulphur, and seems to be 40 times the weight of hydrogen

ARSENIC Certain compounds of Arsenic were known to the ancients It seems to have been known in a distinct character for more than a century Arsenic has a blueish grey colour, and considerable brilliancy, which it soon loses by exposure to the air , its specific gravity is stated to be 8 3 , its fusing point has not been ascertained, by reason of its great volatility it has been heated to 350°, at which temperature it sublimes quickly , and exhibits a strong smell resembling that of garlic, which is characteristic of this metal It combines with oxygen, forming one of the most virulent poisons , also with hydrogen, sulphur, and phosphorus , and it forms alloys with most of the metals

The weight of an atom of arsenic, appears from its compounds to be 42 times that of hydrogen

COBALT The ore of this metal has been long used to tinge glass blue , but it was not till the last century that a peculiar metal was extracted from it Cobalt is of a grey colour, inclining to red , it has not much lustre its specific gravity is about 7 8 , it is brittle , it melts at 180° of Wedgwood , it is attracted

TABLE OF PRODUCTS FORMED BY ACTION OF EXCESS
OF A SOLUTION OF NITRIC ACID ON COPPER.

Temperature, °C	Density of Acid.	NO ₂ (mg.).	N ₂ O ₂ (mg.) (HNO ₂)	NO (a.e.)	N ₂ O (a.e.)
65	1.05		6.45	58.5	2.61
65	1.10		16.02	54.3	3.36
60	1.10		23.4	52.26	4.03
25	1.15		34.15	51.57	1.35
20	1.20		60.49	45.9	
20	1.25		74.16	39.0	
20	1.30	76.7	141.4		
17	1.35	177.9	104.03		
0	1.40	340.5	40.0		
15	1.40	329.9	42.3		
50	1.40	327.9	44.7		

Copper and its salts do not exhibit radioactivity, and have no action on the photographic plate¹

The suggested possibility of transmuting copper into lithium and sodium has already been mentioned (pp 55 and 87)

Valency and Ions—Copper is usually considered to exhibit univalence in the *cuprous* compounds and bivalence in the *cupric* compounds. Its univalence in the cuprous compounds accords with the position of the metal in the periodic system, and is exemplified by the resemblance of the cuprous halides to the halides of silver and univalent gold, and also by the isomorphism of cuprous sulphide and silver sulphide. The bivalence of the atom in the cupric compounds is in agreement with the properties of many of its derivatives, a typical example being the isomorphism of cupric sulphate with the sulphates of ferrous iron, zinc, magnesium, and manganese.

Besides these two main classes of copper compounds, there appear to be other types of copper derivatives, among them oxides of the formulae Cu₄O, Cu₃O, Cu₂O₃, and CuO₂. The *cuprous ion*, Cu⁺, corresponds with the cuprous compounds, which are colourless in aqueous solution. The *cupric ion*, Cu²⁺, corresponds with the cupric compounds, which have a blue, green, violet, yellow, or brown colour in solution.

The cupric ion displays a characteristic power of forming complex derivatives with ammonia² and substituted ammonias, an example being the cupric ammonium hydroxides mentioned on p 254. A great number of other complex derivatives are derived from cuprous or cupric ions. In certain of these compounds both kinds of copper ions are present simultaneously, examples being the complex cupric cuprous

¹ Perman, *Trans Chem Soc*, 1908, 93, 1775.

² Compare Hantzsch and Robertson *Ber* 1908, 41, 4328; 1909, 42, 2135. Dawson, *Ber* 1909, 42, 720. *Trans Chem Soc* 1909, 95, 370. Biltz *Zeitsch physikal Chem* 1909, 67, 561. Poma, *Atti R Accad Lincei*, 1910, [5], 19, 1, 223.

determined from its oxides, seems to be about 40 times that of hydrogen

CHROMIUM This metal, united to oxygen so as to constitute an acid, is found in the *red lead ore* of Siberia The pure metal being obtained, is white inclining to yellow , it is brittle, and requires a great heat to fuse it It combines with oxygen The other properties of this metal are not yet known Its atom, perhaps, weighs about 12 times that of hydrogen

URANIUM This metal was discovered by Klaproth, in 1789, in a mineral found in Saxony It is obtained with some difficulty, and only in small quantities , it has, therefore, been examined but by few The colour of uranium is iron grey , it has considerable lustre , it yields to the file , its specific gravity is 8 1, according to Klaproth , 9 0, according to Bucholz Uranium unites with oxygen, and probably with sulphur its alloys have not been ascertained

The weight of an atom of this metal, is probably about 60 times that of hydrogen

MOLYBDENUM The ore from which this metal is obtained is a sulphuret, called *molybdena* , but it requires an extraordinary heat to reduce it , the metal has not hitherto been obtained, except in small grains It is of a

Applications.—Copper is employed in large quantities in the manufacture of electric conductors and apparatus, and for many other purposes. Its alloys are of the highest importance in the arts, examples being the so-called bronzing powders,¹ brass, gun-metal, coins, and so on.

The effect of copper salts on the growth of wheat has been investigated by Voelcker² for the sulphate and carbonate. Quantities between 0.01 and 0.02 per cent. were found to have a stimulating effect. In smaller proportion the salts were without influence, and in larger amount they exerted a toxic action.

Atomic Weight—The accepted value for the atomic weight of copper, 63.57, is in good accord with the periodic system, the properties of the metal and its compounds being functions of an atomic weight of this order belonging to an element of the fifth horizontal row of Group I of this system. The atomic heat of copper at ordinary temperatures is 5.9 to 6.0, slightly less than the mean value 6.4 for the solid elements, but sufficiently in harmony with the law of Dulong and Petit. The isomorphism of the element with silver and gold, and that of the cuprous compounds with the derivatives of univalent silver, furnish additional evidence in favour of the atomic weight adopted.

Cryoscopic determinations of the molecular weight of copper in solution in other molten metals indicate the monatomic nature of its molecule.

Both chemical and physico-chemical methods have been employed in determining the atomic weight of copper. A summary is appended of the values obtained by both types of process, expressed in terms of the modern notation O=16. The antecedent data employed in the recalculation from the experimental results are

Ag = 107.880	C = 12.003	Na = 22.996
Ba = 137.37	H = 1.00762	S = 32.065
Br = 79.916		

A Chemical Methods—In 1814 Wollaston³ calculated the equivalent of copper to be four times that of oxygen, or Cu=64.

The early researches of Berzelius,⁴ Erdmann and Marchand,⁵ Dumas,⁶ and Millon and Commaille,⁷ involved either syntheses or analyses of cupric oxide, the values found for the atomic weight of copper being 63.30, 63.46, 63.5, and 63.13. Dumas also made syntheses of cuprous sulphide, but gave no details concerning his experiments. His result did not differ much from the modern value, and was adopted for many years.

Hampe⁸ made two series of experiments in 1874. In the first, copper was converted into the basic nitrate, and ignited in a current of

¹ Compare Groschuff *Deut. Mech. Zeit.* 1912 145 153

² Voelcker *J. Roy. Agric. Soc. Engl.*, 1913 74, 411

³ Wollaston *Phil. Trans.* 1814 104 21

⁴ Berzelius *Afhandlingar i Fysik Kemi etc.* Stockholm, 1806–1818, 3 191 6 1
Gilbert's *Annalen*, 1811 37 284 Schuegger's *J.* 1820 30 354 Pogg. *Annalen* 1826

8 182

⁵ Erdmann and Marchand *J. prakt. Chem.* 1844 31 380

⁶ Dumas *Ann. Chim. Phys.* 1859 [3] 55 129

⁷ Millon and Commaille *Compt. rend.* 1863 57 145

⁸ Hampe *Zeitsch. Berg. Hütten und Salinen uesen* 1874 21 218 *Zeitsch. anal. Chem.* 1874 13 354

nitre The atom of titanium probably weighs about 40 or 50 times that of hydrogen

COLUMBIUM In 1802, Mr Hatchett discovered a new metallic acid in an ore containing iron, from America He did not succeed in reducing the acid to a metal, but, from the phenomena it exhibited, there was little room to doubt of its containing a peculiar metal, which he called columbium

TANTALIUM This metal has lately been discovered by M Ekeberg, a Swedish chemist A white powder is extracted from certain minerals which appears to be an oxide of this metal When this white oxide is strongly heated along with charcoal, in a crucible, a metallic button is formed, of external lustre, but black and void of lustre within The acids again convert it into the state of a white oxide, which does not alter its colour when heated to redness

CERIUM The oxide of this metal is obtained from a Swedish mineral No one has yet succeeded completely in reducing this oxide, so that the properties of the metal, and even its existence, are yet unknown But the earth or supposed oxide, is found to have properties similar to those of other oxides These, of course, belong to a future article, the metallic oxides

necessary corrections applied Both the water of crystallization and the copper in the pentahydrate of pure copper sulphate were determined In some of the experiments, after electrolytic deposition of the copper, the sulphuric acid produced in the electrolysis was titrated with pure sodium carbonate, and the sodium sulphate formed was fused and weighed The results were

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	$\text{Cu} = 100$	25 451, whence $\text{Cu} = 63\ 548^*$
CuSO_4	$\text{Cu} = 100$	39 832, " " = 63 597
$\text{Cu Na}_2\text{CO}_3$	= 100	166 838, " " = 63 532*
$\text{Cu Na}_2\text{SO}_4$	= 100	223 525, " " = 63 553*

In one experiment the sulphate was precipitated with barium chloride, and the barium sulphate weighed, but the result is of little value.

Richards also carried out three syntheses of cupric sulphate from the oxide, and two from the metal, deriving the ratios

CuSO_4	$\text{CuO} = 100$	49 838, whence $\text{Cu} = 63\ 548^*$
CuSO_4	$\text{Cu} = 100$	39 7835, " " = 63 468*

Five analyses of cupric oxide by reduction in hydrogen furnished the ratio

$$\text{Cu O} = 79\ 900 \quad 20\ 100, \text{ whence } \text{Cu} = 63\ 602$$

In 1906 Murmann¹ examined the composition of cupric oxide, but his results are of doubtful value Copper oxide formed by heating the metal in oxygen was reduced by hydrogen, and values for the atomic weight varying between 63 513 and 64 397 were obtained Brauner² regards the reduction-method as conducive of high values, but from the results of three oxidations he has calculated that $\text{Cu} = 63\ 53$

In 1913 de Coninck and Ducellez³ converted metallic copper into the nitrate, and ignited the salt to oxide, their value being $\text{Cu} = 63\ 55$

B *Physico chemical Method*—This method consists in determining the electrochemical equivalent of copper with respect to that of silver It involves passing the same quantity of electricity through solutions of cupric sulphate and silver nitrate, and weighing the metal deposited on the cathodes The early researches of (1) Rayleigh and Mrs Sidgwick,⁴ (2) Gray,⁵ (3) Shaw,⁶ and (4) Vanni⁷ gave the results

1	$\text{Cu} \ 2\text{Ag} = 100$	340 561, whence $\text{Cu} = 63\ 354$
2	$\text{Cu} \ 2\text{Ag} = 100$	340 935, " " = 63 25
3	$\left\{ \begin{array}{l} \text{Cu} \ 2\text{Ag} = 100 \\ \text{Cu} \ 2\text{Ag} = 100 \end{array} \right. \begin{array}{l} 389\ 953, \\ 389\ 983, \end{array}$	" " = 63 468
4	$\text{Cu} \ 2\text{Ag} = 100$	340 406, " " = 63 343

During an elaborate investigation of the electrochemical equivalent

¹ Murmann *Monatsh* 1906 27 351

Brauner *Abegg and Auerbach's Handbuch der anorganischen Chemie* Leipzig 1908

² 1 462

³ De Coninck and Ducellez *Revue Chim* 1913 16 122

⁴ Rayleigh and Mrs Sidgwick *Phil Trans* 1884 175 470

⁵ Gray *Phil Mag* 1886 [5] 22 389 1888 [5] 25 179

⁶ Shaw *ibid* 1886 [5] 23 138

⁷ Vanni *Wied Annalen* 1891 [2] 44 214

pounds, or at least to those which consist of *three* atoms, though they may be *binary* in the sense we use the term, and so on to the more complex forms

This chapter will comprehend all the aeriform bodies that have not been considered in the last, several of the acids, the alkalies, the earths, and the metallic oxides, sulphurets, carburets, and phosphurets

In treating of these articles, I intend to adopt the most common names for them, but it will be obvious, that if the doctrine herein contained be established, a renovation of the chemical nomenclature will in some cases be expedient

SECTION I

OXYGEN WITH HYDROGEN

I Water

This liquid, the most useful and abundant of any in nature, is now well known both by analytic and synthetic methods, to be a compound of the two elements, oxygen and hydrogen

Canton has proved that water is in degree compressible. The expansive effect of heat

Atomic Weights The results obtained by Gallo, and by de Coninck and Duceliez, accord reasonably with this number; and those of Shrimpton are in good agreement.

Calculating the foregoing results on the basis $\text{Ag}=107.883$, Brauner¹ has arrived at the value $\text{Cu}=63.56$ from ratios considered by him most trustworthy.

CUPROUS COMPOUNDS²

Cuprous hydride, CuH .—Addition of a concentrated solution of cupric sulphate to a solution of hypophosphorous acid³ or of zinc hypophosphite⁴ yields a powder containing 1.22 per cent of hydrogen, but the chemical individuality of the product is open to question. Berthelot⁵ doubted the possibility of the existence of cuprous hydride, but more recent work has proved his views to be erroneous⁶. The pure hydride can be prepared by the action of sodium hypophosphite on a moderately dilute solution of cupric sulphate at 70° C , but the product formed at ordinary temperature is contaminated with cuprous oxide and cupric phosphate⁷. It is a very unstable, reddish-brown substance, takes fire in chlorine, and is converted by hydrogen chloride into hydrogen, copper, and cuprous chloride. The dry substance cannot be kept for more than twenty-four hours, and at 60° C decomposes suddenly, leaving a sponge of metallic copper.

A very unstable copper hydride of unknown composition has been prepared in the form of a dark-brown powder by Stock and Kuss⁸ by the interaction of cupric sulphate and potassium hypoborate, KH_3OB . It decomposes readily, evolving hydrogen, and leaving a brown residue of metallic copper.

Cuprous fluoride, CuF .—The fluoride has been prepared by the interaction of hydrogen fluoride and cuprous chloride, and also by the dissociation of cupric fluoride, both processes taking place at a high temperature⁹. The product of the action of hydrogen fluoride solution on cuprous oxide¹⁰ appears to be impure copper only¹¹. The fluoride is a ruby-red solid.

Cuprous chloride, CuCl .—The pure chloride is more readily prepared than any other cuprous compound. A summary of the more important methods is appended.

¹ Brauner, *Abegg and Auerbach's Handbuch der anorganischen Chemie*, Leipzig, 1908
², 1 467

² Alloys of copper with silver are mentioned on pp 297 and 301, and with gold on pp 333 and 336. Additional alloys are described in the other volumes of this series. An interesting example of cementation by ferro manganese is given by Sirovich and Cartoceti (*Gazzetta*, 1921 51 II 245). On heating a copper bar at 900° C with powdered ferro manganese and 5 per cent of wood charcoal for some hours, a considerable proportion of manganese was found to have penetrated the copper.

³ Wurtz *Compt rend* 1844 18 702 1879 89 1066 1880 90 22 *Ann Chem Phys* 1844, [3] II, 250

⁴ Schutzenberger *Compt rend* 1869 69 196

⁵ Berthelot *Compt rend* 1879 89 1005

⁶ Mylius and Fromm, *Ber* 1894 27 647 Bartlett and Merrill *Am J Chem* 1912 17 185 Sieverts and Loessner *Zeitsch anorg Chem* 1912 76 1

⁷ Firth and Myers *Trans Chem Soc* 1911 99 1329 *Zeitsch anorg Chem*, 1913 80, 93

⁸ Stock and Kuss *Ber*, 1914 47, 810

⁹ Poulenc, *Compt rend* 1893, 116 1446

¹⁰ Berzelius, *Pogg Annalen*, 1824, I, 28

¹¹ Mauro, *Zeitsch anorg Chem*, 1892, 2, 25, Poulenc, loc cit

place of the incumbent air, and its pressure is found inadequate to restrain the dilatation of the air in the water, which of course makes its escape But it is difficult to expel all the air by either of those operations Air expelled from common spring water, after losing 5 or 10 per cent of carbonic acid, consists of 38 per cent of oxygen and 62 of azote

Water is distinguished for entering into combination with other bodies To some it unites in a small definite proportion, constituting a solid compound This is the case in its combination with the fixed alkalies, lime, and with a great number of salts , the compounds are either dry powders or crystals Such compounds have received the name of *hydrates* But when the water is in excess, a different sort of combination seems to take place, which is called *solution* In this case, the compound is *liquid* and transparent , as when common salt or sugar are dissolved in water When any body is thus dissolved in water, it may be uniformly diffused through any larger quantity of that liquid, and seems to continue so, without manifesting any tendency to subside, as far as is known

In 1781, the composition and decomposition of water were ascertained , the former by Watt and Cavendish, and the latter by Lavoisier

and Carnelley¹ gives 434° C. Carnelley and Williams² give the boiling-point as 954° to 1052° C. For the specific heat Regnault³ found the value 0.1883.

On exposure to light and moisture, cuprous chloride develops a violet or dark blue tint. It also exhibits phototropy when immersed in water slightly acidified with sulphurous acid and subjected to the action of direct sunlight, the colour changing through greyish blue and dark blue to a dark-copper colour, with development of a metallic lustre after a few minutes. In the dark the original white colour is restored in about 48 hours. In absence of moisture the chloride is not sensitive to light, the phenomenon being possibly due to the light inducing the formation of a hydrate unstable in the dark.⁴ In contact with damp air cuprous chloride is converted into a dark-green mixture of cupric chloride and basic cupric chloride. Water transforms it into a mixture of copper, cuprous oxide, and cupric chloride.⁵

Assuming the valency of copper to be unity, the formula for cuprous chloride becomes



Without postulating the univalence of copper, the constitution of the salt can be represented by a double formula



Determinations by Victor Meyer and his collaborators⁶ of the density of gaseous cuprous chloride at 1600° to 1700° C gave values approximately 6.5 times that of the atmosphere. Taking air as unity, the vapour density calculated from the formula Cu₂Cl₂ is 6.83. The close agreement between the two values supports the adoption of the double formula to represent the molecular constitution of gaseous cuprous chloride.

Cryoscopic determinations in dilute solution with pyridine,⁷ quinoline,⁸ and fused bismuth chloride⁹ as solvents have proved the constitution of the salt under these conditions to correspond with the simpler formula Cu-Cl. Solutions in mercuric chloride consist of a mixture of single and double molecules.¹⁰

The conflict of evidence as to the molecular formula of cuprous chloride precludes dogmatic generalization regarding the valency of copper in the cuprous compounds. As a matter of expediency, it seems desirable to assume the univalence of the metal in these derivatives, a view supported by other arguments previously cited (p. 255). To explain the formation of double molecules an interesting assumption

¹ Carnelley *Trans. Chem. Soc.* 1878, 33, 273.

Carnelley and Williams, *ibid.* 1880, 37, 123.

² Carnelley *J. Chem. Phys.* 1841 [3], 1, 129.

³ Regnault *Chem. Soc.*, 1922, 121, 782.

⁴ Lescouet *Ann. Chim. Phys.* 1894 [7], 2, 97; Haywood *J. Physical Chem.* 1897, 1, 411; Bodlander and Storbeck *Zeitsch. anorg. Chem.* 1902, 31, 1, 408.

⁵ Biltz and Victor Meyer *Ber.* 1889, 22, 723; Victor Meyer and Cul Meyer *Ber.* 1879, 12, 609, 1112, 1185, 1292.

⁶ Weinert *Zeitsch. anorg. Chem.* 1897, 15, 560.

⁷ Rubin *Bull. Soc. chim.* 1879 [2], 31, 385.

⁸ Beckmann and Grüber *Zeitsch. anorg. Chem.* 1906, 51, 236.

⁹ Beckmann *ibid.* 1907, 55, 175.

of Volta's eudiometer, an instrument of the greatest importance in researches concerning elastic fluids It consists of a strong graduated glass tube, into which a wire is hermetically sealed, or strongly cemented , another detached wire is pushed up the tube, nearly to meet the former, so that an electric spark or shock can be sent from one wire to the other through any portion of gas, or mixture of gases, confined by water or mercury The end of the tube being immersed in a liquid, when an explosion takes place, no communication with the external air can arise , so that the change produced is capable of being ascertained

The component parts of water being clearly established, it becomes of importance to determine with as much precision as possible, the relative weights of the two elements constituting that liquid The mean results of analysis and synthesis, have given 85 parts of oxygen and 15 of hydrogen, which are generally adopted In this estimate, I think, the quantity of hydrogen is overrated There is an excellent memoir in the 53d vol of the *Annal de Chemie*, 1805, by Humboldt and Gay-Lussac, on the proportion of oxygen and hydrogen in water They make it appear, that the quantity of aqueous vapour which

Other compounds of cuprous chloride include $2\text{CuCl}_2\text{LiCl}$,¹ m.p. 415°C., CuCl_2KCl ,² $2\text{CuCl}_2\text{Ag}_2\text{S}$,³ CuCl_2HgS ,⁴ $\text{CuCl}_2\text{C}_6\text{H}_5\text{NH}_2$, analogous to the ammonia compound cited in the preceding paragraph, and its hydrochloride, $\text{CuCl}_2\text{C}_6\text{H}_5\text{NH}_2\text{HCl}$,⁵ $\text{CuCl}_2\text{C}_6\text{H}_5\text{N}$ and $\text{CuCl}_2\text{C}_6\text{H}_5\text{N}$,⁶ and CuCl_2HCl .⁷

Cuprous bromide, CuBr.—Several methods are available for the preparation of cuprous bromide, examples being the interaction of copper-turnings and an aqueous solution of cupric bromide at its boiling-point,⁸ and the direct synthesis from bromine and excess of copper.⁹ The most convenient process is that of Sandmeyer.¹⁰ A solution of cupric sulphate (12.5 grams), potassium bromide (36 grams), and concentrated sulphuric acid (6 c.c.) in water (80 c.c.) is boiled under reflux with copper-turnings until the solution has become colourless. After precipitation by filtration through asbestos into a large excess of water covered with a layer of ether, the cuprous bromide is allowed to settle. The mother-liquor is then syphoned off, and the salt is washed on a filter with water, alcohol, and ether, and dried in a vacuum-desiccator over sulphuric acid.

The pure bromide is a white substance, but gradually develops a yellow tint, and on exposure to sunlight it acquires a bluish colour⁸. In phototropic character it resembles cuprous chloride, exposure to light changing its colour through dark green to dark copper. If the duration of the action of the light has been limited to a few minutes, keeping in the dark for 30 hours reverses the colour changes¹¹. The melting-point of the bromide is given by Monkemeyer¹² as 480° C., and by Carnelley and Williams¹³ as 504° C. The boiling-point¹³ is between 861° and 954° C., and the density is given by Bodeker¹⁴ as 4.72.

Cuprous bromide is insoluble in water. Its solutions in hydrochloric acid, hydrobromic acid, and ammonium hydroxide readily absorb carbon monoxide. The maximum absorption for the ammoniacal solution corresponds with one molecule of carbon monoxide to each atom of copper.¹⁵ When prepared in absence of air, the solution in ammonium hydroxide is colourless, but on contact with oxygen it develops a blue colour. The liquid obtained by dissolving cuprous bromide in an aqueous solution of sodium chloride or of sodium thiosulphate does not absorb carbon monoxide.

The heat of formation of the simple molecular compound CuBr from solid copper and liquid bromine is 24.985 Cal.¹⁶

¹ Koireng *Jahrb Min Beil Bd*, 1914 37 51 compare Sandonnini *Catetia* 1914
41 1 290

² Korreng loc cit

³ Huntingdon Chem Rev., 1882, 46, 177.

⁴ Raschig, *Ber.*, 1884, 17, 679 Heumann

⁵ Saglier *Compt rend* 1888

⁶ Lang Bei 1892 21 1584

⁷ Neumann *Monatsh.* 1894, 15, 492.

⁸ Renault, *Compt. rend.* 1864, 59, 329; ⁹ Barthélémy, *ibid.* 1865, 59, 324, 381; ¹⁰ G. L. n., *Compt. rend.* 1868,

⁹ Berthimat Ann Chim Phys 1830 [2] 44 224 38
108 1458. Romualdshaus Berg Augsburg 1843 55 316

¹⁸ 1458 Rammelsberg Pogg Annalen 1842 55 246
¹⁹ Sandmeier Ber 1854 17 2659 compare also Borch Gmelin Acad 1859 108 567

¹ Singh *Trans. Chem. Soc.* 1922, 121, 782.

Monkemeyer *Jahrb Min Beil Bd* 1909, 22, 1

¹³ Carnelley and Williams. *Trans Chem Soc* 1880 37 125

¹⁴ Bodeker *Die Beziehungen zwischen Dichte und Zusammensetzung festen und liquiden Stoffen*. Leipzig, 1860.

⁵ Manchot and Friend. *Annalen*. 1908. 359. 100.

¹⁶ Thomsen *Thermochemistry* (Longmans, 1908) 270.

of oxygen unites with one of hydrogen to form one of water Hence, the relative weights of the atoms of oxygen and hydrogen are 7 to 1

The above conclusion is strongly corroborated by other considerations Whatever may be the proportions in which oxygen and hydrogen are mixed, whether 20 measures of oxygen to 2 of hydrogen, or 20 of hydrogen to 2 of oxygen, still when an electric spark is passed, water is formed by the union of 2 measures of hydrogen with 1 of oxygen, and the surplus gas is unchanged Again, when water is decomposed by electricity, or by other agents, no other elements than oxygen and hydrogen are obtained Besides, all the other compounds into which those two elements enter, will in the sequel be found to support the same conclusion

After all, it must be allowed to be possible that water may be a ternary compound In this case, if two atoms of hydrogen unite to one of oxygen, then an atom of oxygen must weigh 14 times as much as one of hydrogen , if two atoms of oxygen unite to one of hydrogen, then an atom of oxygen must weigh $3\frac{1}{2}$ times one of hydrogen

Several complex derivatives of cuprous iodide have been prepared, including $\text{CuI}_2\text{NH}_4^1$, $2\text{CuI}_2\text{NH}_4\text{I}\cdot\text{H}_2\text{O}^2$, $\text{CuI}_2\text{NH}_4\text{I}_4(\text{NH}_4)_2\text{S}_2\text{O}_3^3$, $2\text{CuI}(\text{NH}_4)_2\text{S}_2\text{O}_3\cdot\text{H}_2\text{O}^3$, $2\text{CuI}_2\text{K}_2\text{S}_2\text{O}_3\cdot\text{H}_2\text{O}^3$, and $2\text{CuI}_2\text{Na}_2\text{S}_2\text{O}_3\cdot\text{H}_2\text{O}^3$.

Copper suboxide, Cu_2O — The olive-green precipitate produced by the interaction of solutions of potassium stannite and cupric sulphate⁴ appears not to be the suboxide or quadrantoxide, Cu_4O , but a mixture of cuprous oxide and copper⁵.

Cuprous oxide, Cu_2O — This oxide occurs as the mineral *cuprite* or *ruby copper*. It is formed by reduction of alkaline solutions of complex cupric salts with a reducing sugar, such as dextrose, an example being the reduction of Fehling's solution,⁶ the oxide being deposited as a red, crystalline powder.

Cuprous oxide is produced in the form of an orange-yellow, amorphous gel containing water by the reduction of an alkaline cupric solution with sodium hyposulphite⁷



A better method is the action of hydroxylamine on a cupric salt in presence of alkali⁸. The initial light-yellow product is probably a hydroxide. In absence of air, the colour quickly changes to orange or brick-red, the phenomenon being probably due to elimination of water. The dry product contains 2 to 3 per cent of water, but above low red heat this water is expelled, the metastable, yellow, amorphous oxide becoming transformed into the stable, red, crystalline variety.

Other methods of formation are the addition of sodium carbonate to a solution of cupric sulphate and sodium chloride reduced with sulphurous acid,⁹ and that of an alkaline solution of sodium potassium tartrate to a solution of cuprous chloride and sodium chloride¹⁰. At temperatures below 350° C copper reacts with nitrous oxide to form cuprous oxide, above this temperature the product is cupric oxide¹¹. Cuprous oxide is also formed at the anode in the electrolysis of a solution of cupric sulphate,¹² and by heating cupric oxide in steam.

The oxide crystallizes in cubic octahedra, melting above 1230° C according to Truthe,¹³ and at 1235° C under a pressure of 0.6 mm according to Roberts and Hastings Smyth,¹⁴ and of density 5.75 to 6.09¹⁵. Its solubility in water is very slight, but it dissolves readily in aqueous solutions of ammonia, less readily in potassium hydroxide,¹⁶ and easily in hydrogen halides, with formation of complex derivatives. The

¹ Rammelsberg *Pogg Annalen* 1839 48 162

Sagher *Compt rend* 1887 104 1440

³ Biun *ibid* 1892 114 667

⁴ Rose *Pogg Annalen* 1863 [4] 30 1

Mosc *Zeitsch anorg Chem* 1909 64 200 compare Recoura *Compt rend* 1909

¹⁴⁸ 1105

⁶ Mitscherlich *J prakt Chem* 1840 19 450 Bottger *Annalen* 1841, 39 176

⁷ J *prakt Chem* 1863 90 163

⁷ Moser *loc cit*

⁸ Moser, *Zeitsch anorg Chem* 1919 105 112 compare Paal and Dexheimer *Ber*, 1914 47 219; Suma *Chem News* 1921, 122 99

⁹ Russell *Chem News* 1894 68 308

¹⁰ Groger *Zeitsch anorg Chem* 1902 31 326

¹¹ Sibatier and Sonderens *Compt rend* 1899, 120, 618

¹² Meyer *Bull Soc chim Belg* 1908 22 259

¹³ Truthe *Zeitsch anorg Chem* 1912 76 161

¹⁴ Roberts und Hastings Smyth *J Amer Chem Soc* 1921 43 1061

¹⁵ Compare Clark *Constants of Nature* 2nd ed Washington 1888 1, 54 55

¹⁶ Guntz and Bassett *Bull Soc chim*, 1906 [3] 35 201

Some of the properties of this acid are, 1 In the elastic state it is destructive of combustion, and of animal life, it has a pungent smell, somewhat like muriatic acid, and not less suffocating, its specific gravity has not been accurately obtained, but from some experiments I have made, it seems to be extremely heavy when obtained in glass vessels, in fact, it is in that case a superfluate of silica Into a clean dry flask, I sent a quantity of fluoric acid gas, after some time, the mixture of common air and acid was corked, and the flask weighed it had acquired 12 grains The flask was next inverted in water, to see how much would be absorbed, and that quantity was taken for the acid gas The capacity of the flask was 26 cubic inches, containing originally 8 2 grains of common air, 12 cubic inches of acid gas had entered According to this, if the whole flask had been filled with the gas, it would have gained 26 grains, consequently, 26 cubic inches of the acid gas would weigh 34 2 grains, and its specific gravity be 4 17 times that of common air This experiment was repeated with a proportional result The flask became partially lined with a thin, dry film of fluate of silica during the operation, which no doubt contributed something to the weight, but I am convinced, from other experiments,

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¹ Pammelsberg *Pogg Annalen*, 1839 48 162

³ Brun *ibid* 1892 114 667

² Schlesier *Compt rend* 1887 104 1440

⁴ Rose, *Pogg Annalen* 1863 [4] 30 1

Moser *Zeitsch anorg Chem* 1909 64 200 compare Recouvra *Compt rend* 1909

148 1103

⁵ Mitscherlich *J prakt Chem* 1840 19 400 Bottger *Annalen* 1841 39 176,

J prakt Chem, 1863 90 165

⁶ Moser *loc cit*

⁷ Moser *Zeitsch anorg Chem* 1919 105 112 compare Paal and Dexheimer *Ber* 1914 47 219; Sauer *Chem News* 1921 122 99

⁸ Russell *Chem News* 1894 68 308

¹⁰ Graeber *Zeitsch anorg Chem* 1902 31 326

¹¹ Sibittier und Sendjens *Compt rend* 1895 120 618

¹² Meyer *Bull Soc chim Belg* 1908 22 209

¹³ Truthe *Zeitsch anorg Chem* 1912 76 161

¹⁴ Roberts and Hastings Smyth *J Amer Chem Soc* 1921 43 1061

¹⁵ Compare Cluike *Constants of Nature* 2nd ed Washington 1888 I, 34 35

¹⁶ Gunz and Bassett *Bull Soc chim*, 1908 [3] 35 201

which common air always contains in a diffused state 5 Fluoric acid combines with the alkalies, earths, and metallic oxides, forming salts denominated *fluates*

The weight of an atom of fluoric acid may be investigated from the salts into which it enters as an integral element Of these, the *fluate of lime* is most abundant, and best known Scheele is said to have found 57 parts of lime, and 43 of acid and water, in fluate of lime Richter finds 65 lime, and 35 acid in this salt These are the only authorities I know they differ materially In order to satisfy myself, I took 50 grains of finely pulverized spar, and having mixed with it as much, or more, strong sulphuric acid, the whole was exposed to a heat gradually increasing to redness, the result was, a hard dry crust of mixed sulphate and fluate of lime, this was pulverized, then weighed, and again mixed with sulphuric acid, and heated as before, this process was repeated two or three times, or as long as any increase of weight was found At last, a dry white powder, of 75 grains, was obtained, which was pure sulphate of lime This experiment, two or three times repeated, gave always 75 grains finally Hence, 50 grains of fluate of lime contain just as much lime as 75 grains of sulphate of lime But sulphate of

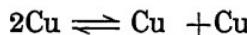
acid and sulphuric acid with decomposition¹ The heat of formation evolved in the direct combination of the elements is 190 Cal²

When suspended in a solution containing both ammonia and ammonium (or other) salts, air at atmospheric pressure oxidizes cuprous sulphide to cupric sulphate and thiosulphate, the reaction being slower than with cupric sulphide In suspension in neutral or acidic solutions, cupric sulphate is produced, the reaction being less energetic than in presence of ammonia, and up to 160° C requiring compressed air³

With sodium monosulphide cuprous sulphide forms a double salt of the formula Na₂S₂Cu₂S⁴ This compound melts at 700° C

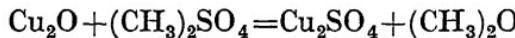
Cuprous sulphite, Cu₂SO₃—Sulphur dioxide reacts with a solution of cupric acetate in acetic acid to form colourless, hexagonal leaflets, Cu₂SO₃. $\frac{1}{2}$ H₂O⁵ In aqueous solution sulphur dioxide converts this substance into a red, prismatic form, Cu₂SO₃.H₂O, also formed by the action of this gas on alkali cuprous sulphites in presence of water⁶ The sulphite is capable of forming complex ammonium derivatives of the type Cu₂SO₃.(NH₄)₂SO₃⁵

Cuprous sulphate, Cu₂SO₄—Cuprous sulphate cannot be isolated by methods analogous to those employed for the preparation of the cuprous halides Metallic copper dissolves in solutions of cupric sulphate containing free sulphuric acid, an equilibrium (or compound) with the scheme



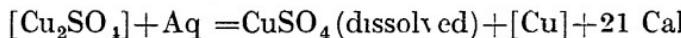
being attained At ordinary temperatures the proportion of cuprous sulphate formed is small, but it is increased by rise of temperature⁷

Cuprous sulphate was first isolated by Recoura⁸ by the interaction of molecular proportions of cuprous oxide and methyl or ethyl sulphate at 160° C in absence of moisture The presence of excess of the alkyl sulphate induces decomposition of the product with formation of cupric sulphate



The salt is dried by washing with ether and placing in a vacuum-desiccator over sulphuric acid

The sulphate is a light grey powder, instantly decomposed by water in accordance with the equation⁹



Since the heat of solution of anhydrous cupric sulphate in water is 158 Cal, the transformation of a gram molecule of cuprous sulphate into cupric sulphate and copper is attended by the evolution of 52 Cal, the reaction being exothermic The formation of cuprous sulphite is an endothermic reaction, although that of each of the other cuprous salts is accompanied by evolution of heat At ordinary temperatures, in presence of dry air, cuprous sulphate is stable, but contact with moist air induces a very slow decomposition The presence of ether tends to

¹ Compare Warlimont *Métaux et Minéraux* 1909 6 83

² Wartenberg *Zeitsch physikal Chem* 1909 67 446

³ Gluud *Ber*, 1922, 55 [B] 952

⁴ Friedrich *Metall und Eisen* 1914 11 79

Ramberg *Zeitsch physikal Chem* 1909 69 512

⁵ Rogojsky *Annalen* 1851 80 255 Étard *Compt rend* 1882 95 36

Foerster and Blankenberg *Ber* 1906 39 4428

⁶ Recoura *Compt rend* 1909 148 1105

⁷ Compare Cundall *Trans Chem Soc* 1914 105 60

that this vapour is the same in quantity for atmospheric air, oxygen, hydrogen, azote, and carbonic acid, and probably for most other gases This vapour can be abstracted from the gases by any body possessing an attraction for water , such as sulphuric acid, lime, &c In short, it can be taken out, as far as is known, by any body that will take out pure steam Some authors consider the vapour united to the air by a slight affinity , others call it hygrometrical affinity, &c My opinion on this subject has already been stated, that the steam mixed with air differs in no respect from pure steam , and, consequently, is subject to the same laws There are some elastic fluids, however, which have so strong an affinity for water, that they will not permit this steam quietly to associate with them , these are fluoric, muriatic, sulphuric, and nitric acids No sooner are these acid gases presented to any air containing steam, but they seize upon the steam , the two united, are converted into a liquid, visible fumes appear, which after playing about a while, are observed to fall down, or adhere to the sides of the vessel, till the gas no longer finding any steam present, occupies the volume of the vessel in a transparent state, free from every atom of vapour These acid gases cannot exist one moment along with

Cuprous carbide or acetylde, Cu₂C₂—The acetylde is formed by the action of acetylene on an ammoniacal solution of cuprous chloride,¹ or on a suspension of cuprous oxide in water.² It is a brownish-red, amorphous substance, and explosive in the dry state.³ Prepared by the first method, it is associated with a molecule of water,⁴ which can be removed by drying over sulphuric acid. The presence of this water has been attributed to adsorption,⁵ and another explanation assumes the compound to have the formula CH≡CCu₂CuOH.⁶ Cuprous acetylde forms complex derivatives with solutions of cuprous chloride and potassium chloride in hydrochloric acid.⁷ Among the examples of those described are the colourless 2CuCl,C₂H₂ and 4CuCl,KCl,C₂H₂, the yellow 8CuCl,2KCl,C₂H₂, and the violet 2CuCl,Cu₂O,C₂H₂. Manchot⁸ found that excess of acetylene combines with cuprous chloride to form white crystals of the formula CuCl,C₂H₂. In presence of hydrochloric acid a dark violet powder of the composition CuCl,C₂Cu₂,H₂O is precipitated. In the dry state this substance is moderately stable. Acetylene combines with excess of cuprous chloride to form white prisms of the composition 2CuCl,C₂H₂.

Cuprous carbonate—Carles⁹ claims to have prepared cuprous carbonate as a glaucous green powder, insoluble in water, by the action of copper on copper carbonate in presence of liquefied ammonia.

Cuprous cyanide, CuCN—Addition of potassium cyanide to a solution of cuprous chloride in hydrochloric acid precipitates cuprous cyanide.¹⁰ The best method for its preparation is to mix cold aqueous solutions of potassium cyanide (65 grams) and cupric sulphate (130 grams), and expel cyanogen by warming the mixture under an efficient air-extractor. After settling, the cuprous cyanide is decanted, and washed with water, alcohol, and ether.¹¹ References to other methods of preparation, and to Sandmeyer's process for aromatic nitriles, are appended.¹²

Cuprous cyanide is a white solid, and is soluble with difficulty in water. It is dissolved readily by cold, concentrated hydrochloric acid, and is reprecipitated from this solvent by addition of an aqueous solution of potassium hydroxide. In contact with air, its colourless solution in ammonium hydroxide develops a blue tint. The salt is also dissolved by aqueous solutions of ammonium chloride, sulphate, and nitrate, and by warm, dilute sulphuric acid. None of its solutions has the power of absorbing carbon monoxide.¹³ The heat of formation of

¹ Berthelot *Ann Chim Phys* 1866 [4] 9 385

² Kaiser *Amer Chem J* 1892 14 285

³ Berthelot *loc cit* With hydrochloric acid cuprous acetylde yields impure acetylene probably contaminated with diacetylene HC≡C—C≡CH (Noyes and Tueller *Amer Chem J* 1897 19, 123)

⁴ Blochmann *Annualen* 1874 173 174

Iebermann and Damrow *Ber* 1892 25 1096

⁵ Schöberl *Ber* 1908 41 3816 compare Mulowla *ibid* 824

⁶ Chavastelon *Compt rend*, 1898 126 1810 127 68 1900 130, 1634, 1764

¹³ 1 48 1901 132 1489

⁷ Manchot *Annualen* 1912 387 257

⁸ Carles *Bull Soc chim* 1915 [4] 17 163

¹⁰ Proust *J de Physique* 1804 59, 350 *Nouveau allegemeines Journal der Chemie* (Gehlen) 1806, 6 573

¹¹ Jacquemin *Bull Soc chim* 1885 [2] 43 556 Valet *Compt rend* 1890,

110 147

¹ Vauquelin *Ann Chim Phys* 1818 9 120 Wohler *Annalen* 1851 78 370

Rammelsberg *Pogg Annalen* 1837 42 124 Sandmeyer *Ber*, 1884, 17, 2650

¹³ Manchot and Friend, *Annalen*, 1908 359, 100

particular, $10\frac{1}{2}$ grains of potassium were burned in 19 cubic inches of fluoric acid, 14 of which disappeared, fluate of potash was formed, and $2\frac{1}{4}$ cubic inches of hydrogen were evolved. Here it is evident, that both oxygen and hydrogen were found in the fluoric acid, and must have made an integral part of that acid, as no vapour could subsist in it, whence it appears, that both oxygen and hydrogen are essential to fluoric acid. Moreover, it is highly probable that the pure acid in the 14 inches of gas, weighed about 6 grains, (common air being $4\frac{1}{2}$) and the oxygen necessary for $10\frac{1}{2}$ potassium, would be 2 grains, whence the acid entering into composition, would be about twice the weight of the oxygen united to the potassium.

I shall now relate some of my own experiments on the decomposition of this acid.

1 Fluoric acid gas may, I find, be kept in glass tubes for several hours or days, without any change of bulk, it continues at the end absorbable by water as at first. Two successive trials were made, by electrifying about 30 water grain measures of the gas. After two hours electrification, no change of volume was produced. Water was then admitted, which absorbed all but 4 grain measures, to this 14 measures of hydrogen were added, and

Cupric fluoride, CuF_2 —Evaporation¹ or precipitation with alcohol² of a solution of cupric oxide or carbonate in excess of hydrofluoric acid yields the fluoride in the form of dihydrate. It crystallizes in small, blue needles, slightly soluble in cold water, and converted by heat into the anhydrous salt. The interaction of gaseous hydrogen fluoride and cupric oxide also produces the anhydrous form as a white solid. It is soluble in mineral acids, is reduced by hydrogen, and is converted into cupric oxide by heating in air. Hot water transforms it into a pale green, slightly soluble *basic fluoride*, $\text{Cu}(\text{OH})_2 \cdot \text{CuF}_2$,¹ a substance also produced by interaction of solutions of cupric sulphate and potassium fluoride.² An *acid salt*, $\text{CuF}_2 \cdot 5\text{HF} \cdot 5\text{H}_2\text{O}$, has also been described.³

Cupric chloride, CuCl_2 —The anhydrous chloride is produced by heating copper or cuprous chloride in chlorine, or by dehydrating the dihydrate by heating at 150°C in an atmosphere of hydrogen chloride,⁴ or by addition of concentrated sulphuric acid to its aqueous solution.⁵ It is a brownish-yellow, hygroscopic solid, melting at 498°C ,⁶ of density 3.054.⁷ It is readily soluble in water and organic solvents. Its heat of formation from its elements, calculated from the interaction of cupric oxide and hydrochloric acid, is given as 51.68 Cal⁸ and 51.4 Cal⁹. It is decomposed by heat into the cuprous salt and chlorine.¹⁰

The *dihydrate*, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, is prepared by evaporating a solution of cupric oxide or carbonate in hydrochloric acid, or by evaporating a solution of cupric sulphate and sodium chloride, the dihydrate crystallizing out after sodium sulphate and chloride, or by addition of barium chloride to a solution of cupric sulphate, filtering, and concentrating. It crystallizes in green, deliquescent, rhombic prisms, but a blue, non-deliquescent form has also been described.¹¹ The density of the dihydrate is 2.47 to 2.535.¹² Its solubility at 17°C is 43.06 grams in 100 grams of water.¹³ A *trihydrate*, $\text{CuCl}_2 \cdot 3\text{H}_2\text{O}$, exists at low temperatures.¹⁴

Numerous basic cupric chlorides have been described, although some of them may not be true chemical compounds.¹⁵ As examples of these substances may be cited the green, rhombic crystals of the mineral atacamite, $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2 \cdot n\text{H}_2\text{O}$, containing a varying proportion of water, the crystalline compound $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$, formed from brown cupric hydroxide and cupric chloride solution,¹⁶ and the compound $\text{CuCl}_2 \cdot 3\text{CuO} \cdot 2\text{H}_2\text{O}$,¹⁷ formed by the interaction of solutions of potassium hydroxide and cupric chloride.

Among the double salts of cupric chloride with other metallic salts

¹ Berzelius *Gmelin Kraut's Handbuch der anorg Chem* 6th ed Heidelberg 1872–1897, 3 648

² Balbiano *Gazzetta*, 1884, 14 74

³ Bohm *Zeitsch anorg Chem* 1905 43 326

⁴ Sabatier *Bull Soc chim* 1895 [3] 13 598

⁵ Vialard *Compt rend* 1902 135 168

⁶ Carnelley *Trans Chem Soc* 1878 33 273

⁷ Playfair and Joule *Mem Chem Soc* 1845 2 401 1848 3 57 Favre and Valson *Compt rend* 1874 79 968

⁸ Thomsen *Thermochimistry* (Longmans 1908), 269

⁹ Berthelot *Thermochimie*, Paris 1897, 2, 319

¹⁰ Rose, *Pogg Annalen* 1836 38 121 ¹¹ Stanford *Chem News*, 1863 7 81

¹² Compare Clarke *Constants of Nature* 2nd ed, Washington 1888, 1, 24

¹³ Reichen and van Devendorf *Zeitsch physikal Chem* 1890 5 559

¹⁴ Chuard *Archives Genève* 1888, [3] 19, 477

¹⁵ Compare Dammer, *Handbuch der anorg Chem*, Stuttgart, 1892–1903, 2, 11 668

¹⁶ Sabatier *Compt rend* 1897 125 101

¹⁷ Miller and Kenrick, *Trans Roy Soc Canada*, 1901–1902, [2] 8 iii 35

and oxygen, and nothing besides as far as is certainly known Now, as the weight of one atom of hydrogen, and two of oxygen, just make 15 times that of hydrogen, there is great reason to presume that this must be the constitution of that acid Besides, analogy is strongly in favour of the conclusion , an atom of the other elementary principles, azote, carbone, sulphur, and phosphorus, joined to two atoms of oxygen, each forms a peculiar acid, as will be shewn in the sequel , why, then, should not one atom of hydrogen and two of oxygen, also form an acid ?

3 *Muriatic Acid*

To obtain muriatic acid in the elastic state, a portion of common salt, muriate of soda, is put into a gas bottle, and about an equal weight of concentrated sulphuric acid , by the application of a moderate heat to the mixture, a gas comes over, which may be exhibited over mercury , it is muriatic acid gas

Some of the properties of muriatic acid gas, are 1 It is an invisible elastic fluid, having a pungent smell , it is unfit for respiration, or for the support of combustion , when mixed with common air, it produces a white cloud,

Cupric iodate, $\text{Cu}(\text{IO}_3)_2$ —Solution of cupric hydroxide or carbonate in a solution of iodic acid yields the iodate, which is known in the anhydrous form,¹ and as monohydrate,² and dihydrate.³ From excess of a solution of potassium iodate, cupric nitrate precipitates the pale blue monohydrate. At 25° C its solubility is 3.3×10^{-3} gram-molecules per litre of water.⁴ A *basic iodate*, $\text{Cu}(\text{IO}_3)_2 \cdot \text{Cu}(\text{OH})_2$, has also been prepared.⁵

Cupric periodates—A number of periodates has been obtained by dissolving cupric hydroxide or carbonate in a solution of periodic acid, and also by the interaction of sodium periodate, NaIO_4 , and solutions of cupric salts.⁶ They have the formulæ $2\text{CuO} \cdot \text{I}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$, $4\text{CuO} \cdot \text{I}_2\text{O}_7 \cdot \text{H}_2\text{O}$, $4\text{CuO} \cdot \text{I}_2\text{O}_7 \cdot 7\text{H}_2\text{O}$, and $5\text{CuO} \cdot \text{I}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$.

Cupric oxide, CuO —This oxide is obtained as a black, amorphous powder by igniting cupric hydroxide, carbonate, or nitrate.⁷ It is also formed on copper anodes in electrolytic oxidation.⁸ The amorphous oxide can be converted into lustrous, cubic tetrahedra by heating with potassium hydroxide,⁹ the crystalline variety being also produced by ignition to redness in a platinum crucible of a small amount of cuprous chloride.¹⁰

A blue variety of cupric oxide is said to have been prepared by precipitating cupric sulphate with sodium hydroxide in presence of dissolved aluminium.¹¹ On heating strongly, it blackens, the change being probably due to an agglomeration of the particles. On the other hand, Muller and Ernst¹² state that agitation of cupric oxide or hydroxide with sodium hydroxide produces a blue precipitate of sodium cuprite. On warming the mixture, this substance dissolves, and on cooling separates in crystals. In contact with excess of water, these crystals decompose to form the black oxide.

Cupric oxide occurs as the hexagonal *tenorite*, and also as the rhombic or monoclinic *melaconite*. According to Slade and Farrow,¹³ the oxide melts above 1148° C , with partial decomposition into cuprous oxide, but Smyth and Roberts¹⁴ state that it does not melt with dissociation below 1233° C . Its density is 6.82 to 6.43.¹⁵ Its mean specific heat is 0.1420 between 12° and 98° C ,¹⁶ and its heat of formation 37.16 Cal.¹⁷

¹ Ditte *Ann Chim Phys*, 1890 [6], 21 173 Granger and de Schulten *Compt rend*, 1904 139 201

² Rammelsberg *Pogg Annalen*, 1838 44 569

³ Millon *Ann Chim Phys* 1843 [3] 9 400

⁴ Spencer *Zeitsch physikal Chem* 1913 83 290

⁵ Granger and de Schulten *Compt rend*, 1904 139 201

⁶ Bengieser *Annalen* 1836 17 254 Langlois *Ann Chim Phys* 1852 [3] 34 257

Lautsch *J prakt Chem* 1867 100 85 Rammelsberg *Pogg Annalen* 1868 134 519

⁷ Vogel and Reischauer *Dingler's Polytech J* 1859 153 197 *Jahresb* 1863, 274

Frdmann and Murchind *J prakt Chem* 1844 31 389

⁸ Muller and Spitzer, *Zeitsch anorg Chem*, 1906 50, 321 Schmidt *Zeitsch Elektrochem* 1908 15 53

⁹ Becquerel *Ann Chim Phys* 1832 51, 101

¹⁰ Schulze, *J prakt Chem* 1880 [2] 21 413

¹¹ Schenck *J Physical Chem* 1919 23 283

¹² Muller and Ernst *Zeitsch angew Chem* 1921 34 371

¹³ Slade and Farrow *Zeitsch Elektrochem* 1912 18 817 compare Wohler and Foss, *ibid* 1906 12 781

¹⁴ Hastings Smyth and Roberts *J Amer Chem Soc* 1920 42 2582

¹⁵ Schroder *Pogg Ann Jubelband* 1874, 452 compare Clarke *Constants of Nature* 2nd ed., Washington 1888 1 55

¹⁶ Regnault *Ann Chim Phys* 1841 [3] 1 129

¹⁷ Thomsen *Thermochemistry* (Longmans, 1908), 268

and five hundred times its bulk of the gas, at the common temperature and pressure, that is, rather less than an equal weight. This combination of water and muriatic acid gas, constitutes the common liquid muriatic acid, or spirit of salt of commerce, but it is never of the strength indicated above. It is usually of a yellow colour, owing to some atoms of iron which it holds in solution.

The constitution of this acid, is a question that has long engaged the attention of chemists. This acid seems more difficultly decomposed than most others. Electricity, so powerful an agent in the composition and decomposition of other acids, seems to fail in this. In the Phil Tr for 1800, Dr Henry has given us the results of a laborious investigation on this subject. From these it appears that pure, dry muriatic acid gas, is scarcely affected by electricity. A very small diminution in volume, and some traces of hydrogenous gas, were observed, which he ascribes to the water or steam which the gas contains. But we have already remarked, (page 283) that muriatic acid gas naturally contains no steam, or, if it contains any, it must be much less than other gases contain. It is probable, therefore, that the hydrogen was derived from the decomposition of part of the acid. This conclusion is strengthened by

(p 269), but more energetic¹ Its heat of formation from its elements is 116 Cal² It dissolves readily in hot, dilute nitric acid, and in solutions of sodium polysulphides³

Copper polysulphides—An orange-red substance of the formula CuS₃ is obtained by fusing cupric sulphate with sodium carbonate and sulphur Heating with carbon disulphide converts it into an amorphous, dark-brown substance, Cu₂S₃⁴ Another polysulphide, Cu₂S₅, is stated to be formed by the interaction at 0° C of a solution of cupric acetate and calcium polysulphide⁵ It has a reddish-brown colour It is doubtful whether any of these polysulphides is a true chemical compound

Cupric sulphite—The normal sulphite is unstable, and has not been isolated With solutions of cupric sulphate sodium sulphite gives a green precipitate of varying composition, but containing basic salts⁶

Cupric sulphate, CuSO₄—The sulphate is prepared by the action of dilute sulphuric acid on cupric oxide or carbonate, the salt crystallizing as *pentahydrate* on evaporation It can also be obtained by dissolving the metal in nitric acid, and decomposing the nitrate by means of sulphuric acid With access of air, the metal is also converted into the sulphate by sulphuric acid

Several methods are applicable to the production of cupric sulphate on the manufacturing scale Old copper plates are heated with excess of sulphur to bright redness in a reverberatory furnace with closed doors until combination is complete The doors are then opened, and the mass is oxidized at dull-red heat When oxidation is complete, the hot product is transferred into dilute sulphuric acid, and the clear solution concentrated after decantation The crystals formed are of a moderate degree of purity The process is also applicable to coarse copper, and to copper-glance and other sulphur ores of copper

When the ores contain iron, it is impossible to separate the ferrous sulphate and cupric sulphate by crystallization If the mixed sulphides are roasted at a suitable temperature, the ferrous sulphate formed is converted into oxide Another method of separation depends on heating a solution of the two sulphates under pressure at 180° C, the ferrous salt crystallizing out⁷ For agricultural purposes the removal of the iron is unnecessary

Crude copper or one of its ores can also be roasted in air, and trans formed into the sulphate by the action of sulphur dioxide⁸

The copper can first be converted into cupric chloride by the action of chlorine and water With sulphuric acid the salt formed reacts to produce cupric sulphite and hydrochloric acid⁹

The formation of cupric sulphate can also be effected by dissolving the oxide in sulphuric acid¹⁰ If the oxide has been produced from an

¹ Glauert Ber 1922 55 [B] 952

² Wittenberg Zeitsch physikal Chem 1909 67 446

³ Rossing Zeitsch anal Chem 1902 41 1

⁴ Rossing Zeitsch anorg Chem 1900 25 407

Bodroux Compt rend 1900 130 1397

⁵ Chevreul Ann Chim Phys 1812 [1] 83 181 Rammelsberg Pogg Annalen 1846 67 397 Scubert and Litton Zeitsch anorg Chem 1893 4 44, Millon and Commaille Compt rend, 1863 57 820

⁶ Gin French Patent 1903 No 328800

⁸ Gin Chem News 1903 88, 554 British Patent 1903 No 5230

⁹ Dariot French Patent 1904 No 350421

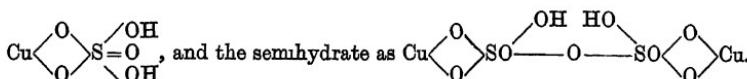
¹⁰ Coste, ibid., 1908, No 392617

form only 14 6 grains of muriate of potash, to which adding 2 grain for the 8 cubic inches of hydrogen, gives 14 8 instead of 19 grains I would therefore adopt the general fact, which was confirmed by several experiments, and is entirely consistent, namely, that *when potassium in sufficient quantity is burned in muriatic acid gas, the whole of the gas disappears, and from one third to one fourth of its volume of hydrogen is evolved, and muriate of potash formed* This is one of the most important facts that has been ascertained, respecting the constitution of muriatic acid Now, the elements of muriate of potash are as follow 35 grains of potassium + 7 of oxygen = 42 of potash , and 12 potash + 22 muriatic acid = 64 grains of muriate of potash From this it appears, that the oxygen in muriate of potash is nearly $\frac{1}{3}$ of the weight of the acid According to this, when potassium is burned in muriatic acid gas, nearly $\frac{1}{4}$ of the whole weight (for the hydrogen weighs little) goes to the oxidizement of the potassium, and the remaining $\frac{3}{4}$ unite with the potash formed Hence, when 22 cubic inches, or 11 grains of gas disappear, as in the particular experiment lately mentioned, $2\frac{3}{4}$ grains nearly must have been oxygen derived from the acid, and $8\frac{1}{4}$ grains of acid joined to the potash so

References to other researches on the solubility of cupric sulphate are appended¹

The investigations of Lescœur² on the vapour-pressure of the hydrates confirm the assumption of the existence of the pentahydrate, trihydrate, and monohydrate MacLeod-Brown³ has suggested two formulæ for the pentahydrate to explain the step-by-step removal of water

A detailed examination of the mechanism of the dehydration of the pentahydrate has been made by Guareschi⁴ Over calcium chloride at 21° to 28° C, or in air at 45° to 50° C, it loses two molecules of water, forming the pale sky-blue trihydrate. In a thermostat at 60° C the trihydrate gives up two more molecules of water, but exposure to air at the ordinary temperature reconverts it into the pentahydrate. The molecule of water present in the monohydrate is expelled at 206° C, and not at 114° C as stated by Pierre, the elimination of the second half taking place slowly. Guareschi regards the monohydrate as having the formula



The heat of formation of the anhydrous salt from its elements is given as 181.7 Cal⁵ and 182.6 Cal⁶

With excess of cupric sulphate reduction with hypophosphorous acid yields metallic copper, but with excess of the acid cuprous hydride is precipitated⁷. Cupric sulphate is also reduced by hydroxylamine⁸.

Copper forms a number of basic sulphates, among them the mineral *langite*, CuSO₄·3CuO·4H₂O, prepared artificially by Sabatier¹⁰ by the interaction of cupric hydroxide and a solution of cupric sulphate. The mineral *brochantite*, 2CuSO₄·5Cu(OH)₂, has been prepared in the laboratory from cupric sulphate solution by the action of limestone¹¹. Shenstone¹² has described a crystalline sulphate, CuSO₄·2Cu(OH)₂. On mixing concentrated solutions of cupric sulphate and ammonium carbonate, and diluting the deep-purple solution, a voluminous, blue precipitate of the formula 15CuO₂SO₃ is produced¹³. Other basic sulphates of this type are 3CuO₂SO₃, 4CuO₂SO₃, 5CuO₂SO₃,

¹ Poggiale, *Ann Chim Phys* 1843, [3] 8 463, Tobler *Annalen*, 1855 95, 193, Brandes and Linhaber *Gmelin Kraut's Handbuch der anorg Chem*, 6th ed Heidelberg 1872-1897, 3 631, Patrick and Aubert *Trans Kansas Acad Sci* 1874 19 Etud *Compt rend* 1887 104 1614 1892 114, 112, *Ann Chim Phys* 1894 [7] 2 503 Cohen *Zeitsch Elektrochem* 1903, 9 433 Cohen Chattaway, and Lombrock, *Zeitsch physikal Chem*, 1907 60 706

² Lescœur *Compt rend* 1886 102 1466, *Ann Chim Phys*, 1890 [6] 21 511 compare Frowen, *Zeitsch physikal Chem*, 1887 1 11, Andicu *ibid* 1891 7, 260 Muller Eizbach, *ibid*, 1896, 19 135

³ MacLeod Brown *Chem News* 1914 109 123

⁴ Guareschi, *Atti R Accad Sci Torino* 1915 50 1125 compare Pierre *Ann Chim Phys* 1846 [3] 16 241 250 Merwin J *Washington Acad Sci*, 1914 4 494

⁵ Berthelot *Thermochimie* Paris 1897, 2, 323

⁶ Thomsen *Thermochemistry* (Longmans, 1908) 324

⁷ Sieverts and Major *Zeitsch anorg Chem*, 1909 64 29

⁸ Adams and Overman *J Amer Chem Soc*, 1909 31 637

⁹ Graham *Annalen* 1839 29 29

¹⁰ Sabatier *Compt rend*, 1897 125 101

¹¹ Bocquerel *Compt rend*, 1852 34 573

¹² Shenstone *Trans Chem Soc* 1885, 47, 375

¹³ Pickering, *ibid*, 1909, 95, 1409

in the same quantity of gas, and then transferring the acid to mercury he observes, ' there was no notable difference in the results ' The inference must, I conceive, be erroneous, 100 cubic inches of muriatic acid gas, united to potash, must give more muriate of potash, than if potassium was burned in the same gas , the weights of the materials necessarily require it , unless it be found that the two muriates are not the same salt

From all the muriates, or salts, into which the muriatic acid enters, it appears (as will be shewn when these salts are considered) that the weight of an atom of muriatic acid is 22 times that of hydrogen Very soon after this determination, it occurred to me that hydrogen was probably the base of the acid , if so, an atom of the acid must consist of 1 atom of hydrogen and 3 atoms of oxygen, as the weights of these just make up 22 In 1807 this idea was announced, and a suitable figurative representation of the atom was given, in the Chemical Lectures at Edinburgh and Glasgow , but this constitution of the acid was hypothetical, till these experiments of Mr Davy seem to put it past doubt The application of the theory to the experiments is as follows on the supposition that the specific gravity of muriatic acid gas is 1 67, it will be found that 12 measures

magnesium sulphate three types are produced at ordinary temperatures almost colourless, rhombic prisms with $7\text{H}_2\text{O}$, light blue, monoclinic crystals with $7\text{H}_2\text{O}$, dark blue, triclinic crystals with $5\text{H}_2\text{O}$ ¹

Complex salts of cupric sulphate with cupric chloride, potassium sulphate, and potassium chloride have been described²

With ammonia, cupric sulphate combines to form complex derivatives Thermochemical data³ indicate the existence of $\text{CuSO}_4 \cdot \text{NH}_3$, $\text{CuSO}_4 \cdot 2\text{NH}_3$, $\text{CuSO}_4 \cdot 4\text{NH}_3$, and $\text{CuSO}_4 \cdot 5\text{NH}_3$. The existence of the complex $\text{CuSO}_4 \cdot 4\text{NH}_3$ has also been postulated from physical measurements⁴ The compound $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ can be prepared by passing ammonia into a solution of cupric sulphate It is stable in dry air⁵ The compound $\text{CuSO}_4 \cdot 5\text{NH}_3$ has been prepared by Rose⁶ and by Mendeleeff⁷

In alcoholic solution cupric sulphate combines with nitric oxide to form a double compound of the formula $\text{CuSO}_4 \cdot \text{NO}$ ⁸

Cupric selenide, CuSe —Hydrogen selenide precipitates cupric selenide from solutions of cupric salts, and it is also produced by the action of selenium vapour on copper⁹ It is a greenish-black substance, of density 6.66

Cupric selenite, CuSeO_3 —At 360° C cupric oxide combines with selenium dioxide to form the selenite as green rods insoluble in water¹⁰

Double Copper Selenates—Tutton¹¹ has investigated the crystallographic properties of double selenates of the series $\text{R}_2\text{SeO}_4 \cdot \text{CuSeO}_4 \cdot 6\text{H}_2\text{O}$, R representing potassium, rubidium, caesium, or ammonium They are isomorphous with the monoclinic double salts formed by cupric sulphate with the sulphates of potassium, rubidium, caesium, and ammonium¹²

Cupric telluride, CuTe —The telluride is stated to be formed by the action of tellurium-powder on a solution of cupric acetate in presence of sulphur dioxide¹³ It can also be precipitated from a solution of sodium telluride, Na_2Te , a sesquitelluride, Cu_2Te_3 , is obtained similarly from the polytelluride Na_4Te_3 (p. 130)¹⁴ A telluride of the formula Cu_4Te_3 occurs as the mineral rickardite

Cupric thiosulphates—Complex cupric alkali thiosulphates have been prepared by Dutoit¹⁵

Cupric dithionate, $\text{CuS}_2\text{O}_6 \cdot 5\text{H}_2\text{O}$ —The triclinic pentahydrate is pre-

¹ Retgers *Zeitsch physikal Chem* 1894 **15**, 571 Hollmann *ibid* 1901 **37** 193 Schincemakers and de Buat *Proc K Akad Wetensch Amsterdam*, 1914, **17**, 333

² Bouzat, *Compt rend* 1902, **135**, 292 534

³ Compare Reyhler *Bull Soc chim* 1895 [3] **13** 387 *Ber* 1895 **28**, 555 Kono willoff *J Russ Phys Chem Soc* 1899 **31**, 910, Immerwahr *Zeitsch anorg Chem* 1900 **24** 269 Dawson and McCrae *Trans Chem Soc* 1900 **77** 1239 1901 **79** 1072 Caus *Zeitsch anorg Chem*, 1900 **25** 236 Perman *Trans Chem Soc* 1902 **81** 487 Bouzat *Compt rend*, 1902 **134**, 1216 *Ann Chim Phys* 1903 [7] **29** 305 Iocke and Lorsdorff *Amer Chem J* 1904 **31** 268 Dawson *Trans Chem Soc* 1906 **89** 1666 Horn *Amer Chem J* 1907 **38** 475

⁵ Horn and Taylor *Amer Chem J*, 1904 **32** 253 compare Horn, *ibid* 1907 **38**, 475 Andree *Compt rend*, 1885 **100** 1138

⁶ Rose *Pogg Annalen* 1830 **20** 150

⁷ Mendeleeff *Ber* 1870 **3** 422

⁸ Münchot *Ber* 1914 **47** 1601

⁹ Little *Annalen* 1859 **112** 378

¹⁰ Espil *Compt rend* 1911 **152** 378

¹¹ Tutton *Proc Roy Soc* 1920 [A] **98** 67

¹ Compare pp 227-230

¹³ Pukman *Jahresbericht* 1861 **126** *Amer Chem J* 1862 [2] **33** 328

¹⁴ Tibbals *J Amer Chem Soc* 1909 **31** 902

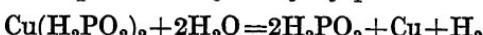
¹ Dutoit, *J Chim phys*, 1913, **11** 650

1 measure, and on letting up water the whole was absorbed, except one measure, which appeared to be hydrogen I sent 700 shocks through a mixture of muriatic acid gas and hydrogen , there was no change A mixture of muriatic acid gas and sulphuretted hydrogen being electrified, hydrogen was evolved, and sulphur deposited, but no change of volume It was evident the sulphuretted hydrogen only was decomposed When a mixture of oxygen and hydrogen is fired along with muriatic acid gas, water is formed, and it instantly absorbs nearly its weight of acid gas From these and such like unsuccessful attempts to decompose the muriatic acid, the importance of Mr Davy's experiments is manifest

The relation of muriatic acid to water must now be considered It has been stated that water at the common temperature and pressure, absorbs 400 or more times its bulk of the acid gas , that is, rather less than its own weight Now, 3 atoms of water weigh 24, and 1 atom of the acid gas weighs 22, it seems probable, then, that the strongest liquid acid that can well be exhibited, is a compound of 1 atom of acid and 3 of water, or contains about 48 per cent acid It is seldom sold of more than half this strength Mr Kirwan's table of the strength

formed by heating cupric chloride in phosphine¹ Other phosphides of the formulæ Cu₅P₂, CuP₂,² and CuP₅³ have been described, but it is doubtful whether they are true chemical compounds

Cupric hypophosphite, Cu(H₂PO₂)₂—The solution obtained by addition of slightly less than the equivalent proportion of barium hypophosphate to a solution of cupric sulphate yields, after removal of the barium sulphate and addition of alcohol, the hypophosphite in the form of white crystals⁴ At ordinary temperatures the dry salt does not decompose for several days, but at 90° C it explodes with evolution of phosphine On warming in aqueous solution, it decomposes with formation of phosphorous acid, copper, and hydrogen Its aqueous solution is also decomposed catalytically by palladium



Cupric phosphite, CuHPO₃.2H₂O—A phosphite of this formula is obtained by the interaction of solutions of diammonium hydrogen phosphite and cupric chloride, or of phosphorous acid and cupric acetate⁵ It is unstable, but admits of drying at a medium temperature

Cupric orthophosphate, Cu₃(PO₄)₂.3H₂O—The orthophosphate is prepared by the interaction of disodium hydrogen phosphate and excess of cupric sulphate,⁶ or by heating an aqueous solution of orthophosphoric acid with cupric carbonate at 70° C⁷ It is a blue, crystalline powder, almost insoluble in water

The *basic orthophosphate*, Cu₃(PO₄)₂.Cu(OH)₂, occurs as *libethenite* in the form of dark green crystals, produced artificially by heating the orthophosphate with water⁷ In combination with two molecules of water it also occurs as *tagilite*

Cupric pyrophosphate, Cu₂P₂O₇—The anhydrous salt is precipitated as a greenish-white powder by addition of sodium pyrophosphate to a solution of a cupric salt⁸ The *pentahydrate* crystallizes from a solution containing cupric sulphate and sodium metaphosphate⁹

Cupric metaphosphate, Cu(PO₃)₂—The metaphosphate is formed by evaporating to dryness an aqueous solution of cupric nitrate and orthophosphoric acid, and heating the residue at 316° C¹⁰ The *tetrahydrate* is prepared by precipitating with alcohol a solution of cupric sulphate and sodium metaphosphate¹¹

Cupric arsenites—A pigment of varying composition is prepared as a canary-green precipitate by mixing solutions of an alkali metal arsenite and cupric sulphate¹² It is known as *Scheele's green* Other cupric derivatives of arsenious acid are also known¹³

¹ Rose *Pogg Annalen*, 1826, 6 206 1832, 24 295 compare Bottger *Jahresbericht* 1857, 107

Rubenowitch, *Compt rend* 1898, 127, 270 1899, 129 336 Granger *ibid*, 1895, 120 923, 1896 122 1484

² Bossuet and Hackspill *ibid*, 1913 157, 720

⁴ Engel *ibid*, 1899 129 518

⁵ Rose *Pogg Annalen* 1828 12, 291 Wurtz *Ann Chim Phys*, 1846 [3], 16, 199

Rummelsberg *Pogg Annalen* 1867 132 491

⁶ Steinschneider *Dissertation* Halle 1890

⁷ Debruy *Ann Chim Phys* 1861 [3], 61, 439

⁸ Persoz *ibid*, 1847 [3] 20 315 Fleitmann and Henneberg *Annalen* 1848, 65 387

⁹ Wiesler *Zeitsch anorg Chem*, 1901 28 201

¹⁰ Maddrell *Annalen* 1847 61 60 ¹¹ Fleitmann *Pogg Annalen* 1849 78 242

¹² Bloxam *J Chem Soc* 1862 15 281

¹³ Reichard, *Ber* 1894 27, 1019 Stavenhagen, *J prakt Chem* 1895 [2] 51, 1

contain so many grains of pure acid , the third contains the grains of acid in 100 water grain measures , this is convenient in practice to prevent the trouble of weighing the acid , the fourth contains the specific gravity of the liquid acid , and the fifth contains the temperature at which acids of the various strengths boil This last is entirely new, I apprehend , it shews a remarkable gradation of temperature the strong acid boils at a moderate heat , as the acid weakens , the boiling temperature rises till it gets to 232° , after which it gradually drops again to 212° When an acid below 12 per cent is boiled, it loses part of its quantity, but the remainder, I find, is concentrated , on the other hand, an acid stronger than 12 per cent is rendered more dilute by boiling It appears from a paper of Dr R Percival in the 4th vol of the Irish Transactions, that in the ordinary process of manufacturing the muriatic acid, the middle product is usually of the strength which boils at the maximum temperature , but the first and last products are much stronger The reasons for these facts will probably be found in the gradation of temperature in the above column

commercial copper carbonate to be similar in constitution to malachite, a view questioned by Dunnichoff and Lal¹

Sodium hydrogen carbonate and cupric sulphate react to precipitate a blue, basic carbonate, $5\text{CuO}, 3\text{CO}_2, n\text{H}_2\text{O}$, converted by drying at 100° C into another blue hydrate, $5\text{CuO}, 3\text{CO}_2, 7\text{H}_2\text{O}$. Another basic carbonate is also produced in the same reaction. It has the formula $8\text{CuO}, 3\text{CO}_2, 6\text{H}_2\text{O}$, is dark blue in colour, and becomes green at 100° C . No other basic carbonate was isolated by Pickering. All the products are insoluble in water and sodium-carbonate solution, but dissolve slightly in solutions of carbon dioxide and of sodium hydrogen carbonate, with production of the normal carbonate or a double carbonate.

Feist² has prepared a basic carbonate, $7\text{CuO}, 4\text{CO}_2, \text{H}_2\text{O}$, by powdering together crystallized cupric sulphate and sodium carbonate, and then adding water. It is difficult to separate the substance from a basic cupric sulphate simultaneously formed. Auger³ has described an amorphous basic carbonate of the formula $8\text{CuO}, 5\text{CO}_2, 7\text{H}_2\text{O}$. Another basic carbonate, $7\text{CuO}, 2\text{CO}_2, 5\text{H}_2\text{O}$, has been prepared⁴ by the interaction of a mixture of sodium carbonate and sodium hydrogen carbonate with cupric sulphate in aqueous solution. Complex carbonates of copper with sodium and potassium have also been obtained⁵. An example of this type of double salt of the formula $\text{Na}_2\text{Cu}(\text{CO}_3)_2, 3\text{H}_2\text{O}$ crystallizes on addition of a solution of cupric acetate to one of sodium carbonate and sodium hydrogen carbonate at 50° C ⁶. It forms needles or rosette-like agglomerations, and above 100° C it is converted into cupric oxide and sodium carbonate with elimination of water and carbon dioxide. It is decomposed by water, but can be recrystallized from a concentrated solution of sodium carbonate containing sodium hydrogen carbonate.

Cupric cyanide, $\text{Cu}(\text{CN})_2$.—The cyanide is obtained as a brownish-yellow precipitate by the interaction of solutions of potassium cyanide and cupric sulphate, but it is very unstable, decomposing at ordinary temperatures into *cupric cuprous cyanide*, $\text{Cu}[\text{Cu}(\text{CN})_2]_2, 5\text{H}_2\text{O}$, with evolution of cyanogen. On heating, it is converted into cuprous cyanide. With hydrazine cyanide it unites to form a *monohydrazine*, $\text{Cu}(\text{CN})_2, \text{N}_2\text{H}_4$, yellow needles insoluble in water, m p 160° to 162° C ⁷.

Cupric thiocyanate, $\text{Cu}(\text{CNS})_2$.—The thiocyanate is formed as a velvet-black precipitate by adding basic cupric carbonate or cupric hydroxide to a solution of thiocyanic acid, and by the interaction of potassium thiocyanate and concentrated solutions of cupric salts⁸. It is very unstable, being transformed by contact with water into cuprous thiocyanate⁹. With ammonium hydroxide it yields blue, acicular crystals of *ammonio cupric thiocyanate*, $\text{Cu}(\text{CNS})_2 \cdot 2\text{NH}_3$, also produced by dissolving cupric hydroxide in ammonium thiocyanate¹⁰.

Cupricsilicates.—The emerald-green, hexagonal *dioptase*, $\text{CuSiO}_3, \text{H}_2\text{O}$, has the density 3.28 to 3.35. The turquoise-blue *chrysocolla* has density

¹ Dunnichoff and Lal *Trans Chem Soc* 1918 113 718

Feist *Arch Pharm* 1909 247 439

² Auger *Compt rend* 1914 158 944

Dunnichoff and Lal *loc cit*

Pickering *Trans Chem Soc* 1909 95 1409 1911 99 800

³ Appleby and Lane *ibid* 1918 113 609

Franzen and Lucking *Zeitsch anorg Chem* 1911 70 145

⁴ Meitendorff *Pogg Annalen* 1842 56 63. Soderbacl (*Annalen*, 1919 419, 217) prepared it by the action of thiocyanogen (p. 320) in ether solution on cuprous thiocyanate.

⁵ Claus *J prakt Chem* 1838 15 403

⁶ Grossman, *Zeitsch anorg Chem* 1908 58 265

temperature of 60° and common pressure of pure gas, water takes up about twice its bulk of the gas. If the gas be diluted with air, then much less is absorbed, but the quantity is not proportionate to the abstract pressure of the gas, as is the case with those gases mentioned at page 201. Thus, if the pressure of oxymuriatic acid gas be $\frac{1}{7}$ th of atmospheric pressure, water will be found to take up $\frac{2}{3}$ ds of its bulk, which is more than twice the quantity it ought to take by the rule of proportion. Hence it is evident, that the absorption of this gas by water, is partly of a mechanical and partly of a chemical nature.

3 Water impregnated with the gas is called liquid oxymuriatic acid. It has the same odour as the gas, and an astringent, not acid, taste. When exposed to the light of the sun, the liquid acid is gradually decomposed, as was first observed by Berthollet, into its elements, muriatic acid and oxygenous gas, the former remains combined with the water, and the latter assumes the gaseous form. Neither light nor heat has been found to decompose the acid gas.

4 This acid, in the gaseous state or combined with water, has a singular effect on colouring matter. Instead of converting vegetable blue into red, as other acids do, it abstracts colour.

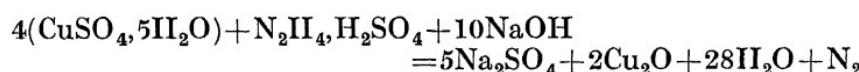
deposition of the metal from an acidic¹ or alkaline² solution. It can also be estimated by precipitation as acetylide from ammoniacal, neutral, or slightly acidic solutions of cupric salts³. Another method depends on reduction to copper by hypophosphorous acid or alkali hypophosphite, and ignition to cupric oxide⁴. Hydroxylamine hydrochloride has also been suggested as a reagent for its estimation⁵.

Numerous volumetric methods for the estimation of copper have been described. Volhard's process consists in reducing with sulphurous acid in presence of a slight excess of ammonium thiocyanate, the copper being precipitated as cuprous thiocyanate, and the excess of ammonium thiocyanate estimated by titration with silver nitrate in presence of a ferric salt as indicator⁶. Parkes's method depends on titration of a blue cupric-ammonia solution with standard potassium cyanide, the endpoint of the reaction being indicated by the disappearance of the colour. Stannous chloride can also be employed in the volumetric estimation of copper, a boiling solution of cupric chloride in concentrated hydrochloric acid being titrated with this reagent until the yellow colour of the solution is discharged. In Haen's method an acetic acid solution of the cupric compound is mixed with excess of potassium iodide, and the free iodine estimated with standard thiosulphate. Another process involves conversion of the copper into cuprous thiocyanate, and titration of this salt with potassium iodate⁷. Chloroform is added to dissolve the iodine initially liberated, and the completion of the reaction is marked by the disappearance of the violet colour of the solution.



References to other methods are appended⁸.

A gasometric method for the estimation of cupric salts is based on the reduction of cupric ammonia solutions by a hydrazine salt, a cuprous-ammonia solution being formed, and the hydrazine oxidized to nitrogen and water.



The volume of the evolved nitrogen can be measured,⁹ or its weight can be determined by means of an apparatus similar to that employed by von Schrotter in the estimation of carbon dioxide.¹⁰

¹ Focster *Ber* 1906 39 3029 *Zeitsch Elektrochem*, 1907 13 561 Hawley *Fing and Min J* 1920 110 162

² Spitzer *Zeitsch Elektrochem* 1905 11 345 391 Flamigen *J Amer Chem Soc* 1907 29 455

³ Sodderbaum *Ber* 1897 30 902 3014

⁴ Dallimore *Pharm J* 1909 [4] 29 271 compare Hanus and Soukup *Zeitsch anorg Chem* 1911 70 282 Cuvillié *Boll chim Farm* 1912 51 437 Windisch *Zeitsch anal Chem* 1913 52 1 619 Hanus *ibid* 616

⁵ Bayer *Zeitsch anal Chem* 1912 51 729

⁶ Compare Theodor *Chem Zeit* 1908 32 889 Kuhn, *ibid* 1056

⁷ Jimieson Levy and Wells *J Amer Chem Soc* 1908 30 760

⁸ Gooch and Wurd *Amer J Sci* 1909 62 348 Bacovescu and Vishuta *Ber* 1909 42 2638 A summary of the applications of organic compounds to the estimation of copper and of other metals has been given by Chaston Chapman (*Trans Chem Soc* 1917 III 203)

⁹ Ebler *Zeitsch anorg Chem* 1905 47 371

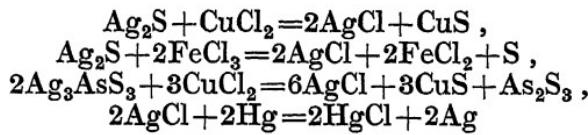
¹⁰ de Saporta *Rev gen Chim pure et appl* 1907, 10, 338, Pozzi Escot *Bull Assoc chim Sucr Dist* 1908 26 267

obtained, the one a simple muriate, and the other a hyperoxygenized muriate, in which an acid with an enormous quantity of oxygen is found, and is hence called *hyperoxymuriatic acid*

7 One very remarkable property of oxymuriatic acid has recently occurred to me in a course of experiments upon it Cruickshanks had found that if hydrogen and oxymuriatic acid gases were mixed together, and kept in a well stopped bottle for 2½ hours, when the stopper was withdrawn under water, the gases disappeared, and water took their place Being desirous to ascertain the time more definitely, I made the mixture in a narrow eudiometer, and left it to stand over water, in about three quarters of an hour the greater part of the mixture had disappeared In the next experiment, the gases, after being put together, seemed to have no effect for one or two minutes, when suddenly the mixture began to diminish with rapidity, like one of common air and nitrous gas, except that there were no red fumes The diminution went on, till in two or three minutes *nearly* the whole had disappeared On repeating the experiment a few hours afterwards no such diminution was observed I recollect that the sun had shone upon the instrument in the former one, it was

before amalgamation into the chloride, effected by roasting with common salt, or by the action of common salt and copper compounds at the ordinary summer temperature

In the *patio process* the finely ground ore is mixed in a *patio* or paved courtyard with mercury, common salt, and a mixture of copper and iron sulphates called *magistral*, prepared by roasting copper pyrites. The ore-heap or *torta* is kept moist. The reactions involved are obscure and complex, but it is supposed¹ that some of them can be represented thus



The process of amalgamation requires from a fortnight to a month. The amalgam is decomposed by heating in retorts.

The *pan-amalgamation process* has found more favour than the *patio* process. The ore in the form of fine sludge is stirred in iron pans with a mixture of mercury, common salt, and cupric sulphate. When the action is complete, the excess of mercury is drained off, and the amalgam is allowed to settle, and then decomposed by heat. In the *Boss system* the process is continuous, a series of pans and settlers being employed. Some silver ores, notably those containing sulphides of arsenic, antimony, copper, iron, and zinc, are roasted with common salt before amalgamation.

Among the older methods is the *cauldron* or *cazo process* for ores free from sulphur. The ore was reduced by boiling with a solution of common salt in copper vessels, and then amalgamated. In the *Franketina process* sulphide ores were roasted with common salt, and then boiled with a solution of salt in presence of mercury in copper bottomed vessels. In the *Kronke process* decomposition of the ore is effected by a hot solution of cuprous chloride and common salt, reduction to metallic silver and amalgamation being effected by addition of mercury and in amalgam of lead or zinc. In the obsolete *Freiberg barrel process* sulphide ores were roasted with salt, and amalgamated in rotating barrels with mercury, iron being added to prevent formation of mercury chlorides.

(2) LIXIVIATION

The silver is dissolved from the ore by an aqueous solution of a salt, and then precipitated as metal or sulphide. The *cyanide process*² is the most important of the lixiviation methods, its application having been considerably extended in recent years, especially in Mexico. The ore is very finely crushed with cyanide solution in a stamp mill, and the sludge produced submitted to agitation and aeration in contact with cyanide solution. The liquid is separated from the ore by the aid of mechanical filters, and the silver precipitated from the clear solution by addition of zinc in the form of dust or shavings. The product is smelted with nitre, and is sometimes refined by blowing air through the molten mass.

¹ Vondráček, *Rev de Metallurgie* 1908 5, 678

² Caldecott, *J Chem Met Mining Soc S Africa* 1908 8 203 266

filled with water when the stopper was drawn out under water , but it generally happened that the stopper was expelled with violence

It remains now to point out the constitution of this acid All experience shews, that it is a compound of muriatic acid and oxygen , but the exact proportion has not hitherto been ascertained Berthollet, who investigated the subject by impregnating water with the acid gas, and then exposing it to the solar rays till the oxygen was liberated, found it to consist of 89 parts of muriatic acid, and 11 of oxygen, by weight Whether all the oxygen is liberated in this way is more than doubtful , the quantity of oxygen is certainly much underrated Chenevix makes 84 muriatic acid and 16 oxygen to constitute this acid , he too has the oxygen too low , probably because he estimated *all* the salt formed by this acid to be simple muriate, or hyperoxymuriate , but there is no doubt that oxymuriate does exist in the mixture, because it possesses the property of bleaching Of all the authors I have seen, Cruickshank comes the nearest to the truth , he says, 2 measures of hydrogen require 2 3 measures of oxymuriatic acid to saturate them , and it is known that they require 1 of oxygen , hence he infers, that 2 3 measures of this acid gas contain 1 measure of oxygen From this

lead by successive additions of zinc, the argentiferous zinc rising in crusts to the surface, and being ladled off. After liquation to remove some of the lead, the zinc is distilled from a retort, the residue consisting of lead and about 5 to 10 per cent of silver. Where a demand for zinc sulphate exists, the zinc is also converted into this salt by oxidation with steam and solution in sulphuric acid.

Cupellation is effected by oxidizing the argentiferous lead in a reverberatory furnace with a hearth of bone-ash, marl, magnesia, or Portland cement and crushed fire brick, the litharge formed being kept liquid by maintaining the temperature above 900° C. The litharge and the oxides of other base metals flow to the edge of the bath of molten metal, and are drawn off. By cupellation it is possible to obtain silver containing only 0.2 per cent of impurities, but it has often to be cupelled again with more lead. Different types of cupellation-furnace are employed in Great Britain, the United States, and Germany.

In the electrolytic refining of copper (p. 249) both silver and gold are deposited in the insoluble sludge at the bottom of the vessel, and are subsequently extracted from this sludge, the silver being dissolved by boiling with sulphuric acid, and subsequently precipitated by copper.

Refining—Various methods are employed in refining silver. The process of parting it from gold is described on p. 326. In addition to gold, the principal impurities are copper, iron, lead, and zinc.

Physical Properties—Silver is a white, lustrous metal, and in very thin layers has a violet colour by transmitted light, in thicker layers the colour is purple¹. Such layers are produced by depositing a silver mirror on glass by the action of sodium potassium tartrate on an ammoniacal solution of silver nitrate². Reduced silver in the form of a fine powder has a grey, earth-like appearance³. The metal crystallizes in octahedra belonging to the cubic system. The density of the unrolled metal is 10.4923, that of the metal after rolling, 10.5034⁴. Its melting-point is given as 958.3° C.⁵, 960° C.⁶, 960.5° C.⁷, 960.9° C.⁸, 961° C.⁹, 961.5° C.¹⁰ and 962° C.¹¹, and its boiling point as 1955° C.¹² and 2040° C.¹³ at 760 mm. With the exception of gold, it is the most malleable and ductile of the metals, and can be hammered into leaves 0.0025 mm thick. Its conductivity for heat and electricity is higher than that of any other substance. Its specific heat is given as 0.05535,¹⁴ 0.0557,¹⁵ and

¹ Houllier *Compt rend.*, 1909, 149, 1368 compare Turner *Proc Roy Soc* 1908 [A] 81, 301

(Compare Kohlschutter *Annalen* 1912, 387, 86)

² Compare Pisarewsky, *J Russ Phys Chem Soc* 1908, 40, 367 *Zeitsch anorg Chem* 1908, 58, 399

³ Kuhlbaum Roth und Siedler *ibid* 1900, 33, 353

Day and Clement *Amer J Sci* 1908 [4], 26, 405

⁴ Day and Sosman *ibid* 1910, [4], 29, 93

⁵ Heycock and Neville *Trans Chem Soc* 1895, 67, 1024 Durr and Foot, *Trans Faraday Soc* 1920, 15, 186

⁶ Wadner und Burgess *Bull Bureau Standards* 1909, 6, 149

⁷ Guertler und Pianini *Zeitsch Metallurgie* 1919, 11, 1

⁸ Quercigh *Zeitsch anorg Chem* 1910, 68, 301

⁹ Berthelot *Ann Chim Phys* 1902, [7], 26, 58

¹⁰ Greenwood *Zeitsch Elektrochem* 1912, 18, 319 *Proc Roy Soc* 1909 [A] 82

¹¹ 396 compare *ibid* 1910 [A] 83, 483

¹² Hinsen *Ber* 1909, 42, 210 compare von Waatenberg *Zeitsch anorg Chem* 1908, 56, 320

¹³ Bronsted *Zeitsch Elektrochem* 1912, 18, 714

¹⁴ Schimpff *Zeitsch physikal Chem*, 1910, 71, 257, compare Magnus *Ann Physik*, 1910, [4], 31, 597 Richards and Jackson, *Zeitsch physikal Chem* 1910, 70, 414

methods always deposit some brown oxide of manganese when treated with ammonia, but that obtained by the last deposits none. The action of muriatic acid on hyperoxymuriate of potash, evidently consists in detaching the superfluous oxygen from the compound, and not the hyperoxymuriatic acid particle from the particle of potash.

As the oxymuriatic acid is of great and increasing importance in a theoretical as well as practical point of view, I have spent much time in endeavouring to ascertain the proportion of its elements, and have, I think, succeeded, at least, I am pretty well satisfied myself as to its constitution. The methods I have taken are both synthetical and analytical, but I chiefly rely upon the latter.

I filled a eudiometer with dry mercury, and sent up 13 water grain measures of muriatic acid gas, to which were added 9 measures of oxygenous gas of 77 per cent purity, which consequently consisted of 7 oxygen and 2 azote. The instrument had platinum wires. About 1300 small electric shocks were passed through the mixture of gases, a gradual diminution ensued, the mercury became foul, the same as when oxymuriatic acid is in contact with it. The 22 measures were reduced to 4, which were not diminished by washing. To these 4

preparation, and partly on the age of the specimen¹. Reduction of the monoxide by 60 per cent formaldehyde at 85° C yields a very stable solution of colloidal silver, varying in colour from pale-lilac to rich ruby-red.² The effect is not produced by employing acetaldehyde. In presence of Irish moss, hydrazine hydrate yields colloidal silver varying in colour from dark-reddish brown to brownish yellow in transmitted light. The more dilute solutions thus prepared are very stable, and can be kept for two months. By this means it has been found practicable to prepare solutions containing 17 per cent of colloidal silver, but such concentrated forms lack stability.³ The colloidal solution decomposes hydrogen peroxide slowly.

Colloidal silver can also be prepared by forming an electric arc between silver poles immersed in water, the solutions being brown with a low current, and green with a stronger current.⁴ The electric conductivity of the solution produced by the second method is higher than that of the brown solution. Addition of an electrolyte also converts the brown solution into the green form.⁵ The conductivity of such solutions has been attributed to the presence of silver oxide.⁶

When silver is boiled with water for a prolonged period, a colloidal solution is formed. It contains 0.0162 gram of silver per 100 c.c.⁷ Another procedure involves heating the metal to redness or a higher temperature and plunging it into cold water.⁸ Many other methods of preparing colloidal silver have been described.⁹

Plates of copper or zinc precipitate colloidal silver from solution.¹⁰ The solid forms are brittle, and amalgamate with mercury. Acids convert them into grey silver, without evolution of gas.

A therapeutic preparation of colloidal silver is known as "collargol." Credc's ointment also contains this form of silver, and is employed in the treatment of certain types of septic infection. An astringent antiseptic is prepared by the action of an alkaline tannin solution on aqueous solutions of silver salts.¹¹

In photography colloidal silver plays an important part, an instance being the image produced in the ordinary printing-out process.

Neither the metal nor any of its salts displays radioactivity.¹²

Chemical Properties—At the ordinary temperature silver is stable

¹ Compare Henriot *Compt rend.*, 1903, 137, 122 Bancroft *J. Physical Chem.*, 1919, 23, 554.

² Pickles *Chem. News*, 1918, 117, 358.

³ Utbier Wolf and Kress *Kolloid Zeitsch.*, 1922, 30, 31.

⁴ Biedig *Zeitsch angew. Chem.* 1898, 11, 951.

⁵ Compare Woudstra *Zeitsch physikal. Chem.* 1908, 61, 607. Lottermoser *ibid.* 62, 284. Rebicci *Compt rend.* 1912, 154, 1540.

⁶ Rebicci *Compt rend.* 1909, 148, 354.

⁷ Iitube Mengarini and Scali *Att. R. Accad. Lincei* 1909, [5], 18, 1, 542.

⁸ Kimura *Mem Coll Sci Eng Kyōto* 1913, 5, 211.

⁹ Schneider *Ber.* 1891, 24, 370. 1892, 25, 1164. 1281. 1440. Batus and Schneider *Zeitsch physikal. Chem.* 1891, 8, 278. Wied *Annalen* 1893, 48, 357. Oberbeck *ibid.* 745. Lottermoser and Meyer *J. prakt. Chem.* 1897, 56, 241. 1898, 57, 540. Lottermoser *ibid.* 1905, 71, 296. Blake *Amer. J. Sci.* 1903, 16, 282. Chassavant *Bull. Soc. chim.*, 1904, 31, 11. Paul *Ber.* 1902, 35, 2206. Kuspert *Ber.*, 1902, 35, 2815. 4066. 4070. Gutbier and Hofmeier *Zeitsch anorg. Chem.* 1905, 45, 77. Castoro *Gazzetta* 1907, 37, 1, 391. *Zeitsch. Chem. Ind. Kolloide* 1910, 6, 283. Kohlschütter *Zeitsch. Elektrochem.* 1908, 14, 49. *Zeitsch. Chem. Ind. Kolloide* 1913, 12, 285 (summary). Pieroni *Gazzetta* 1913, 43, 1, 197.

¹⁰ Philipson *Zeitsch. Chem. Ind. Kolloide* 1912, 11, 49.

¹¹ Sensburg *German Patent* 1909 No 208189.

¹² Levin and Ruer *Physikal. Zeitsch.*, 1909, 10, 576.

of hydrogen require $3\frac{1}{2}$ of the acid to saturate them I have found the results a little different , but the error is not much, and is what might be expected Whether we treat oxy-muriatic acid over mercury or water, we are sure to lose some of it , and unless the loss can be estimated and allowed for, we are apt to overrate the acid required Before the action of light on this mixture was discovered, I used to mix known quantities of the two gases together, in a graduated eudiometer of Volta, over water , and, after letting the mixture stand a few minutes, in order to a complete diffusion, I passed a spark through, but noticed the moment before at what degree the mixture stood , in this way, when there is an excess of hydrogen, the results are accurate , the total diminution can be found, and the residuary gas can be analyzed to find the hydrogen left, and the common air (if any), which is extremely apt to be found in a greater or less degree, in all oxymuriatic acid obtained over water By frequent careful trials, I found that a measure of hydrogen required as near as possible an equal measure of the acid to saturate it But since the effect of solar light was discovered, I have operated in a more simple and elegant manner , and the results appear rather more uniform and accurate I

$215.94 = 2 \times 107.97$ ($O=16$) In 1808 Dalton preferred the value $Ag=100$ ($O=7$), in 1817 Meinecke selected $Ag=108$, and in 1826 Gmelin gave the same value for the equivalent of the metal

In the section on the atomic weight of sodium (p 87) mention is made of the close relationship between the atomic weight of this element and the atomic weights of silver, potassium, chlorine, bromine, and iodine. In the sections on the atomic weights of sodium and potassium (*loc cit*, and p 155) an outline of the general principles underlying the methods adopted by the earlier investigators in determining the atomic weights of these elements is given, and the experimental results of a number of researches are summarized. Here it will suffice to describe the determination of ratios not previously mentioned. As with sodium and potassium, the experimental work naturally falls into two main divisions (1) that of the early investigators, and (2) that carried out under the extremely accurate conditions required of modern atomic-weight research.

In connexion with the early work, only a summary of results need be given. The values for the various ratios $AgXO_3 / AgX$ are stated in the table.

Experimenter	Year	Ratio
Marignac ¹	$AgClO_3 / 3O = 100$	x
	1843	$x = 25.083 \pm 0.0041$
Stas ²	1865	$= 25.0795 \pm 0.0010$
		Mean (Clarke) $= 25.0797 \pm 0.0010$
Stas ³	$AgBrO_3 / 3O = 100$	x
	1865	$x = 20.349 \pm 0.0014$
Millon ⁴	$AgIO_3 / 3O = 100$	x
	1843	$x = 17.047 \pm 0.005$
Stas ⁵	1865	$= 16.9747 \pm 0.0009$
		Mean (Clarke) $= 16.9771 \pm 0.0009$

Determinations of the ratios Ag / AgX are more numerous. The next table summarizes the results.

¹ Marignac *Oeuvres complètes* Geneva 1902 I 80

Stas *Oeuvres complètes* Brussels 1894 I 645

² Stas *ibid* 635

³ Millon *Ann Chim Phys* 1843 [3] 9 400

⁴ Stas *Oeuvres complètes* Brussels 1894, I 628

oxymuriatic acid gas to convert them into water In every one of the experiments, the acid was less than the hydrogen

The above experiments are highly amusing in a day of clouds and gleams, the presence of the direct solar light instantly gives the motion of the mercury a stimulus, and it as quickly abates when a cloud intervenes The surface of the mercury in the tube always becomes fine sky blue during the process, and so does liquid ammonia that has been used to decompose oxymuriatic acid, I do not know what is the reason in either case

From the results above, it appears that 100 measures of oxymuriatic acid gas must consist of 53 measures of oxygen, united to a certain portion of muriatic acid gas Now, 100 cubic inches of oxymuriatic acid gas weigh 72 or 73 grains, and 53 inches of oxygen weigh about 18 grains, which is rather less than $\frac{1}{4}$ th of the above Hence, if the atom of muriatic acid weigh 22, that of oxymuriatic acid must weigh 29, and thus we obtain the constitution of this last acid An atom of it consists of one of muriatic acid and one of oxygen united, the former weighs 22, the latter 7, together making 29, or about 76 muriatic acid, and 24 oxygen, per cent Thus, it appears, that the former experiments on the specific gravities of

For silver sulphate Stas¹ found the percentage of silver to be $69\ 203 \pm 0\ 0012$, and Struve's² result was $69\ 230 \pm 0\ 004$. According to Clarke, the weighted mean is



Computation of the atomic weight of silver from the data cited involves a knowledge of the mean values for the ratios KCl : O, KBr : O, KI : O, NaCl : O, Ag : KCl, Ag : KBr, Ag : KI, and Ag : NaCl, as determined by the early workers. These values are given in the sections on the atomic weights of sodium and potassium (pp 87 and 155). The two early determinations of the ratios RX : AgX lack accuracy, and are omitted.

Combination of the various ratios gives

$$\frac{\text{KCl}}{3\text{O}} \times \frac{\text{Ag}}{\text{KCl}} = \frac{\text{Ag}}{3\text{O}} \quad \text{Ag} = 107\ 927 \pm 0\ 0106 \quad (1)$$

$$\frac{\text{KBr}}{3\text{O}} \times \frac{\text{Ag}}{\text{KBr}} = \frac{\text{Ag}}{3\text{O}} \quad \text{Ag} = 108\ 196 \pm 0\ 0837 \quad (2)$$

$$\frac{\text{KI}}{3\text{O}} \times \frac{\text{Ag}}{\text{KI}} = \frac{\text{Ag}}{3\text{O}} \quad \text{Ag} = 107\ 666 \pm 0\ 0278 \quad (3)$$

$$\frac{\text{NaCl}}{3\text{O}} \times \frac{\text{Ag}}{\text{NaCl}} = \frac{\text{Ag}}{3\text{O}} \quad \text{Ag} = 107\ 919 \pm 0\ 0079 \quad (4)$$

$$\frac{\text{AgCl}}{3\text{O}} \times \frac{\text{Ag}}{\text{AgCl}} = \frac{\text{Ag}}{3\text{O}} \quad \text{Ag} = 107\ 939 \pm 0\ 0050 \quad (5)$$

$$\frac{\text{AgBr}}{3\text{O}} \times \frac{\text{Ag}}{\text{AgBr}} = \frac{\text{Ag}}{3\text{O}} \quad \text{Ag} = 107\ 930 \pm 0\ 0092 \quad (6)$$

$$\frac{\text{AgI}}{3\text{O}} \times \frac{\text{Ag}}{\text{AgI}} = \frac{\text{Ag}}{3\text{O}} \quad \text{Ag} = 107\ 906 \pm 0\ 0062 \quad (7)$$

$$\text{Ag}_2\text{S} \times \left\{ \left(\frac{2\text{Ag}}{\text{Ag}_2\text{S}} \times \frac{\text{Ag}_2\text{SO}_4}{2\text{Ag}} \right) - 1 \right\} = \frac{4\text{O}}{2\text{Ag}} \quad \text{Ag} = 107\ 962 \pm 0\ 0090 \quad (8)$$

Results (2) and (3) differ sufficiently from the others to compel their rejection. The arithmetic mean of the other six results is Ag=107.93. With the exception of (4), they depend mainly on the work of Stas, and when his results only are employed in the calculations the same mean value is obtained, but the individual results are more concordant.

Despite the agreement of these results, they are now known to be very erroneous,³ although the value Ag=107.93 was given in the International Atomic Weight Committee's table down to 1908. The probability of the correct result being nearer to 107.89 or 107.88 was inferred by Guye⁴ in 1905 as a necessary consequence of changing the

¹ Stas *Ouvres complètes*, Brussels 1894, I, 410
Struve *Annalen* 1851, 80, 203

² For criticisms of the work of Stas reference should be made to the papers by Richards and others cited later particularly the paper by Richards and Wells. Compare also Dumuis *Ann. Chim. Phys.* 1878 [5] 14, 289; Stas *Ouvres complètes*, Brussels 1894, 3, 106; Dubreuil *Compt. rend.* 1908, 147, 856, 1300; *Bull. Soc. chim.* 1909, [4], 5, 260, 313, 341, 1049; Leclerc *Compt. rend.* 1908, 147, 972; 1909, 148, 42; Hinrichs *ibid.* 1908, 147, 1302.

³ Guye *Arch. Sci. phys. nat.* 1905 [4], 20, 351; *Bull. Soc. chim.* 1905 [3], 33, 1, *J. Chim. phys.* 1906, 4, 174; *Chem. News* 1906, 93, 35; Guye and Ler Gazzanai *Compt. rend.* 1906, 143, 411; Guye and Germann, *J. Chim. phys.*, 1916, 14, 204.

alkalies and earths, by sending a stream of oxymuriatic acid gas into solutions of these elements, or of their carbonates in water. The acid combines with the alkali, but in process of time, as the solution becomes concentrated, a change takes place in the acid, one atom of oxymuriatic acid seizes upon an atom of oxygen from each of its neighbouring particles, and reduces them to ordinary muriatic acid, in this state it forms with an atom of alkali an hyperoxymuriate, whilst the other atoms of acid form muriates. It seems that the oxymuriates are difficultly attainable, because, as their solutions are concentrated, they are so apt to be resolved and compounded again, as above.

Berthollet first pointed out the peculiarity of this acid but its nature and properties were more fully discussed by Hoyle in 1797, and by Chenevix in 1802. These authors made their principal experiments on hyperoxymuriate of potash, they nearly agree as to the constitution of the salt, but differ in some of the circumstances of its production. It yields by heat about 2 or 3 per cent of water, about 38 per cent of oxygen, and 59 or 60 of a salt unalterable by heat, which Chenevix considers as simple muriate, but Hoyle says it exhibits traces of oxymuriatic acid by sulphuric acid

$$\frac{30}{\text{KCl}} \times \frac{\text{KCl}}{\text{Ag}} = \frac{30}{\text{Ag}} = 0.64382 \times 0.691069,$$

$$= 0.444924,$$

$$= 48.107884,$$

Ag = 107.884

or

A similar method of calculation can be applied to the results of Richards and Willards's analyses of lithium chloride and lithium perchlorate, as indicated in connexion with the atomic weight of lithium (p. 57), it gives *Ag = 107.871*

Another calculation of the atomic weight of silver can be made from modern determinations of the ratios $2\text{Ag} : \text{I}_2\text{O}_5$ and $\text{Ag} : \text{I}$

$$\frac{\text{I}}{\text{Ag}} \times \left\{ \left(\frac{\text{I}_2\text{O}_5}{2\text{Ag}} \times \frac{\text{Ag}}{\text{I}} \right) - 1 \right\} = \frac{50}{2\text{Ag}}$$

The iodine-pentoxide ratio was very carefully determined by Baxter and Tilley¹ in 1909 to be

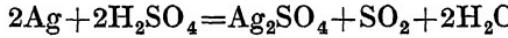
$$\text{I}_2\text{O}_5 : 2\text{Ag} = 100 : 64.6230,$$

and the composition of silver iodide was found by Baxter² in 1910 to be

$$\text{Ag} : \text{I} = 100 : 117.6601$$

Combination of the two ratios gives the value *Ag = 107.864*

In 1913 Scheuer³ dissolved silver in sulphuric acid, collected and weighed the sulphur dioxide evolved, and dried, fused, and weighed the silver sulphate



The weights are in the ratios $2\text{Ag} : \text{Ag}_2\text{SO}_4 : \text{SO}_2$, and the atomic weight of silver is readily calculated, since

$$\frac{2\text{Ag}}{\text{Ag}_2\text{SO}_4 - 2\text{Ag} - \text{SO}_2} = \frac{2\text{Ag}}{2\text{O}}$$

The mean of five experimental results gave *Ag = 107.884*

The modern values for the atomic weight of silver vary between 107.864 and 107.884. The current table of the International Committee on Atomic Weights gives *Ag = 107.88*, but possibly 107.87 is a better approximation to the true value, as has been pointed out by Guye.⁴ As an essential factor in the calculation of many other atomic weights, the atomic weight of silver is of fundamental importance.

ALLOYS AND COMPOUNDS OF SILVER

Alloys⁵ A description of various alloys of silver with copper and with gold⁶ has been given by several authors⁷. British silver coin and stan-

¹ Baxter and Tilley / *Trans. Chem. Soc.* 1909, 31, 201.

Baxter *ibid.* 1910, 32, 1591; compare Baxter *ibid.* 1904, 26, 1577; 1905, 27, 876.

² Scheuer *Arch. Sci. phys. nat.* 1913 [4], 36, 381.

³ Guye *J. Chim. phys.* 1917, 15, 549; 1919, 17, 171.

For silver amalgam see this series Vol. III.

⁴ Compare pp. 297, 301, 333 and 336.

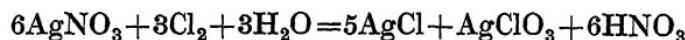
⁵ Kurnakoff und Schmitschusny *J. Russ. Phys. Chem. Soc.* 1908, 40, 1067; Lepkowsky *Zeitsch. anorg. Chem.* 1908, 59, 285; Kurnakoff Puschin and Senkowski, *J. Russ. Phys. Chem. Soc.* 1910, 42, 733; *Zeitsch. anorg. Chem.* 1910, 68, 123; Wardner and Burgess *Bull. Bureau of Standards* 1909, 6, 149; Janecki *Zeitsch. angew. Chem.*, 1912, 25, 935 (summary of previous work); Raydt *Zeitsch. anorg. Chem.* 1912, 75, 58.

and 25 of the latter Hoyle does not inform us on this head, Chenevix found 84 of the former and 16 of the latter. Here then is some obscurity. The fact, I believe, is, that there is always a greater or less portion of real oxymuriate of potash amongst the salts formed, or in the mass which Chenevix calls the *entire salt*. Oxymuriatic acid precipitates silver from nitrate as well as muriatic, and as this was the test, it is evident Chenevix must have confounded a quantity of oxymuriate of potash with the muriate. The quantity may even be ascertained. For, if 25 75 16 48 In 100 of Chenevix's entire salt, there were then 16 hyperoxymuriate, 48 muriate, and the rest or 36 must have been oxymuriate. Hoyle's experiments confirm this conclusion, for, he observes that the remaining muriate (after the hyperoxymuriate was abstracted) was considerably oxygenized, since with the addition of acids it became a powerful destroyer of vegetable colours. This could not be the case with a muriate, nor even a mixture of muriate and hyperoxymuriate. Besides, it is well known that the oxymuriate of potash (or oxymuriatic acid absorbed by potash) was largely used for the purpose of bleaching, now if the acid had immediately resolved itself into muriatic and

phous precipitate of silver chloride, which can be converted into a crystalline form by evaporating its solution in concentrated hydrochloric acid or ammonium hydroxide. The native variety is known as *horn-silver*, and crystallizes in the cubic system. Its density is 5.31 to 5.55. The crystalline form is also produced by slow diffusion of a solution of hydrogen chloride into one of silver nitrate. Its cubic crystals are isomorphous with those of silver bromide.¹

The melting-point of amorphous silver chloride is given as 451° C.,² 452° C.,³ and 455° C.,⁴ the substance fusing to a yellow liquid. After solidification its density is 5.45 to 5.59. The specific heat is 0.08775.⁵ At 18° C. its solubility⁶ is 1.17×10^{-5} gram-molecules per litre of water, and at 25° C., 1.6×10^{-5} . Silver chloride also dissolves in solutions of ammonia,⁷ sodium thiosulphate, potassium cyanide, mercuric nitrate, and in concentrated hydrochloric acid and saturated chloride solutions. For the heat of formation from the elements Berthelot gives 29.2 Cal., and Thomsen⁸ 29.38 Cal. Wolff⁹ considers their results too low, and gives the value 30.612 Cal., that stated by Braune and Koref¹⁰ being 30.41 Cal. The intermediate value 29.940 Cal. is given by Fischer.¹¹

Chlorine reacts with an aqueous solution of silver nitrate to form chloride and chlorate of silver, the hypochlorite being an intermediate product.



Silver chloride absorbs gaseous ammonia, forming double compounds of the composition $2\text{AgCl}, 3\text{NH}_3$ and $\text{AgCl}, 3\text{NH}_3$. The first crystallizes in rhombic plates from ammoniacal solutions of silver chloride,¹² the second is formed in long prisms by heating the chloride with a saturated aqueous solution of ammonia under pressure.¹³ The dissociation-pressure of these compounds have measurable values.¹⁴ Other compounds of similar type with the formulae $\text{AgCl}, 3\text{NH}_3$ (9.16), $\text{AgCl}, 1\frac{1}{2}\text{NH}_3$ (10.52), and AgCl, NH_3 (11.11) have also been prepared,¹⁵ the figures in parentheses giving the calculated heats of formation in large calorics. The interaction at 200° C. of iodic acid and ammoniacal solutions of the chloride to form silver iodide has been the subject of investigation.¹⁶ A cold ammoniacal solution of sodium peroxide reduces silver chloride,¹⁷ and it is also reduced to the metal by the action of zinc in the course of a

¹ Kurnakoff and Schemtschuschny *J. Russ. Phys. Chem. Soc.* 1908 **40** 1067
Schemtschuschny *ibid.* 1916 **48** 203

² Monkmeyer *Jah. Min. Bel. Bd.* 1909 **22** 1

³ Pruthi *Zeitsch. anorg. Chem.* 1912 **76** 161

⁴ Brønsted *Zeitsch. Elektrochem.* 1912 **18** 714 compair Magnus *Ann. Phys.* 1910

[4] 31 597

⁵ Holloman *Zeitsch. physikal. Chem.* 1893 **12** 125 Kohlrausch und Rose *ibid.* 234 compair Hill *J. Amer. Chem. Soc.* 1908 **30** 65 Kohlrausch *Zeitsch. physikal. Chem.* 1908 **64** 129 van Rossem *Chem. Weekblad* 1912 **9** 396

⁶ Compair Petter *Ber.* 1908 **41** 3175

⁷ Thomson *Thermochimistry* (Longmans 1908) 254

⁸ Wolff *Zeitsch. Elektrochem.* 1914 **20** 19

⁹ Braune und Koref *Zeitsch. anorg. Chem.* 1914 **87** 175

¹⁰ Fischer *Zeitsch. Elektrochem.* 1912 **18** 283

¹¹ Kunc *Ann. Chim. Phys.* 1840 **72** 290

¹² Leclerc *Compt. rend.* 1884 **98** 1279

¹³ Isambert *ibid.* 1868 **66** 1529 Horstmann, *Ber.*, 1876 **9** 749 Biltz *Zeitsch. physikal. Chem.* 1909 **67** 561

¹⁴ Biltz and Stollenwerk *Zeitsch. anorg. Chem.* 1920 **114** 174

¹⁵ Baudigny *Compt. rend.* 1908 **146** 1097

¹⁶ Booth, *Chem. News* 1911, **103**, 288

nished, but only a small quantity, that when no fumes appear, no diminution takes place, they hence conclude, that this acid gas is an excellent test of the presence of hygrometric water [steam] in gases, and observe that all gases contain such, except fluoric, muriatic, and probably ammoniacal Berthollet, Jun has proved the last mentioned gas to contain no combined water, and Gay-Lussac and Thenard suspect it contains none hygrometrically, but some experiments of Dr Henry convince me that it does, and I think its not fuming when mixed with common air is a proof of it — They observe, that when water is saturated with fluoric acid gas, it is limpid, smoking, and extremely caustic, that heat expels about one fifth of the acid, and the remainder becomes fixt, resembling concentrated sulphuric acid, and requiring a high temperature to boil it They query from this fact, whether sulphuric and nitric acid are not naturally gasiform, and owe their liquidity to the water combined with them They exposed a drop of water to 60 cubic inches of fluoric acid gas, the drop, instead of evaporating, was increased in volume by the absorption of the acid, and hence they conclude, that fluoric acid gas is also free from combined water, the conclusion is extended to ammoniacal

photochlorides are characterized by their great sensitiveness to light, blue light producing a blue coloration, and red light a red coloration. This action is reversible, the blue coloration being transformed into red by the action of red light, and so on. This phenomenon is inapplicable to the production of colour-photographs, for white light causes a darkening in colour.

There are several theories as to the constitution of the silver subhalides in the latent image. The *molecular theory* regards the subhalides as definite chemical compounds. The *adsorption theory* regards them as adsorption-compounds of colloidal silver and subhalides. The molecular theory is advocated by Trivelli,¹ who considers the colour-changes to indicate the existence of several silver subhalides, which yield solid solutions with each other and with the silver halides. He also regards the mechanism of "reduction" with ammonium persulphate as favouring the molecular theory.

Light reacts with silver halides, producing a series of subhalides containing a diminishing proportion of halogen, the colour-changes taking place for all the halides in the sequence green, bluish-green, blue, violet, red, orange, yellow.² Guareschi³ has noted that the darkening of silver salts by light was observed before the time of Boyle (1668), and that investigations made by Schulze (1727), Beccari (1757), and Scheele (1777) were very important for the development of photography. In a more recent paper, Boruttau⁴ states that the colour changes undergone by silver salts under the influence of light were first mentioned by Konrad Gessner in 1565 in his work *De omni verum fossilium genere libri aliquot*, where the darkening of native horn-silver is cited. Hydrogen peroxide has no action on silver bromide, but with the green, blue, or red photohalide oxygen is immediately evolved, with formation of silver bromide and silver monoxide.⁵

Luppo Cramer prefers the adsorption-theory because the red, blue, or violet photohalides are formed from the hydrosols of the silver halides in presence of colloidal silver by precipitation with any electrolyte, and treatment of the resulting gel with nitric acid. He attributes the action to adsorption of colloidal silver by the gel of the normal silver halide. He states that identical silver halides are produced by the action of light on silver chloride and bromide, and regards the assumption of the existence of subhalides as unjustifiable.⁶ An investigation of the action of light on silver halides has been made by Huitung⁷ with the aid of the microscope, and has furnished evidence in support of Luppo Cramer's view. On exposure to light and air, silver bromide loses 24 per cent of its total bromine, its colour changing from pale yellow to pale purple, but exposure to the action of bromine in absence of light restores the original colour, the initial weight being regained almost completely. In air, silver chloride loses 41 per cent of its chlorine, and in vacuum 81.0 per cent, the original weight being restored by the action of

¹ Trivelli *Zeitsch wiss Photographie* 1908 6, 358 438

² Trivelli *Proc K Akad Wetensch Amsterdam*, 1909 11 730

³ Guareschi *Atti R Accad Sci Torino* 1914 49 1083

⁴ Boruttau *Zeitsch angew Chem* 1918 31 139

⁵ Trivelli *Chem Weekblad* 1909 6 525 compare Trivelli *ibid* 1910 7 321 404

Zeitsch wiss Photographie 1911 9 185

⁶ Luppo Cramer *Zeitsch angew Chem* 1909 22 2330 compare Luppo Cramer, *Zeitsch Ind Kolloide* 1910 6 7 168 7 42 99 304, 1911, 8 42

⁷ Huitung *Trans Chem Soc*, 1922 121, 682

They seem to think that the acid is decomposed in this case but they have not advanced any opinion, that either fluoric or muriatic acid gas consists entirely of hydrogen and oxygen

SECTION 2

OXYGEN WITH AZOTE

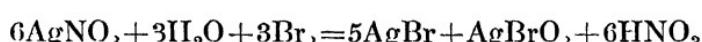
The compounds of oxygen with azote, hitherto discovered, are five, they may be distinguished by the following names, nitrous gas, nitric acid, nitrous oxide, nitrous acid, and oxynitric acid In treating of these, it has been usual to begin with that which contains the least oxygen, (nitrous oxide) and to take the others in order as they contain more oxygen Our plan requires a different principle of arrangement, namely, to begin with that which is most simple, or which consists of the smallest number of elementary particles, which is commonly a binary compound, and then to proceed to the ternary and other higher compounds According to this principle, it becomes necessary to ascertain, if possible, whether any of the above, and which of them, is a binary compound As far as the specific

iodic acid into the iodide¹. Double compounds with ammonia of the formulæ AgBr_3NH_3 (8.64), $\text{AgBr}_1\frac{1}{2}\text{NH}_3$ (9.95), and AgBr_2NH_3 (10.65) have been prepared,² the figures in parentheses indicating the calculated heats of formation in large calories.

The action of light is similar to that on silver chloride, *silver photobromide* being produced with liberation of bromine.³ The change in weight under the influence of light does not exceed 2.4 per cent.⁴ Silver bromide is more sensitive to light than any other substance, and is extensively employed in the manufacture of dry photographic plates. The glass is coated with an emulsion produced by addition of ammoniacal silver nitrate to a solution of potassium bromide containing gelatin, the mixture being digested at 40° to 45° C for about an hour to increase the size of the bromide granules.⁵ The emulsion is solidified by cooling with ice, washed with water, liquefied, and poured over the glass. It is usual to add a small proportion of silver iodide as a decelerator, and a slight excess of potassium bromide to eliminate silver nitrate.

A short exposure in the camera to light produces the "latent image," the process being attended by slight reduction, and the formation of photobromide, probably a solid solution of silver and silver subbromide in silver bromide.⁶ The latent image is developed by immersing the plate in an alkaline reducer, such as pyrogallol or quinol, in presence of alkali. The reduction takes place first at those points where it has been initiated by the action of light. Development must not be continued so long as to cause general blackening of the plate or "chemical fog." When it is complete, the image is "fixed" by dissolving the unaltered silver salt in a solution of sodium thiosulphate. The velocity of reduction is lowered by the presence of bromine ions, so that the operator can control the rate of reduction by addition of a solution of potassium bromide to the developer.

Collodion can be substituted for gelatin in the preparation of the emulsion, but the plates are less sensitive than the gelatin plates. Gelatin exerts a reducing action on silver bromide, but collodion does not, the collodion plates are consequently free from the trace of fog characteristic of gelatin plates, and therefore give a very sharp, well-defined image suitable for technical reproduction. Collodion plates are rendered more sensitive by the presence of silver nitrate in the emulsion, but such plates have to be exposed in the wet condition, and are not well adapted for field work. The increase in sensitiveness depends on the reaction:



Silver bromide is most sensitive to blue light, but can be rendered sensitive to the green, red, and ultra-red portions of the spectrum by dyeing the emulsion with members of the eosin group or the cyanine

¹ Bubigny *Compt rend* 1908 146 1097

² Blitz und Stollnwerk *Zeitsch anorg Chem* 1920 114 174

³ On the liberation of bromine by sunlight compare Schwarz and Stock *Ber* 1921

54 [B] 2111

II - *Trans Chem Soc*, 1922 121 682, compare Koch and Schrader, *Zeitsch Physik* 1921 6 127

⁵ Cohen *Eder's Jahrbuch* 1895 103 Fder *Handbuch der Photographie* Halle 1893 Part III Abegg and Herzog *Arch wiss Phot* 1900 1 115 Baur and Postius *Physikal Zeitsch* 1902 3 491

⁶ Compare Weisz *Zeitsch physikal Chem* 1906 54 305

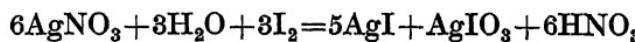
	Sp gr	constitution by weight	Ratios	
Nitrous gas 1	102	46 6 azote + 53 4 oxy	6 1 7	Davy
	44 2	— + 55 8 —	5 5 7	
	42 3	— + 57 7 —	5 1 7	
Nitr oxide 1	61 4	63 5 — + 30 5 —	2 × 6 1 7	Cavendish
	62	— + 38 —	2 × 5 7 7	
	61	— + 39 —	2 × 5 4 7	
Nitr c acid 2	41 4	29 5 — + 70 5 —	5 8 7 × 2	Cavendish
	29 6	— + 70 4 —	5 9 7 × 2	
	28	— + 72 —	5 4 7 × 2	
	25 3	— + 74 6 —	4 7 7 × 2	

The above table is principally taken from Davy's Researches where two or more results are given under one article, they are derived from different modes of analysis In the third column are given the ratios of the weights of azote and oxygen in each compound, derived from the preceding column, and reduced to the determined weight of an atom of oxygen, 7 This table corroborates the theoretic views above stated most remarkably The weight of an atom of azote appears to be between 5 4 and 6 1 and it is worthy of notice, that the theory does not differ more from the experiments than they differ from one another, or, in other words, the mean weight of an atom of azote derived from the above experiments would equally accommodate the theory and the experiments The mean is 5 6, to which all the others might be reduced We should then have an atom of nitrous gas to weigh 12 6, consisting of 1 atom of azote and 1 of

as 13.8 Cal,¹ 14.3 Cal,² 14.57 Cal,³ 15.1 Cal,⁴ 15.158 Cal,⁵ and 15.17 Cal.⁶

Silver iodide is only slightly soluble in ammonia, but dissolves in sodium thiosulphate, concentrated hydriodic acid, and saturated solutions of potassium iodide.⁷ It forms a series of double salts with silver bromide,⁸ with mercuric iodide,⁹ and with the iodides of the alkali metals.¹⁰ Double compounds of silver iodide and ammonia of the formulæ $\text{AgI},3\text{NH}_3$ (6.92), $\text{AgI},1\frac{1}{2}\text{NH}_3$ (7.25), AgI,NH_3 (8.56), $\text{AgI},2\text{NH}_3$ (7.05), and $\text{AgI},\frac{1}{2}\text{NH}_3$ (11.59) have also been prepared,¹¹ the figures in parentheses indicating the calculated heats of formation in large calories.

Like the other silver halides, silver iodide is sensitive to light, the loss in weight not exceeding 1.1 per cent.¹² The sensitiveness to light is diminished by the presence of potassium iodide, and increased by that of silver nitrate. In the second instance the liberated iodine reacts with the silver nitrate.



The possibility of developing the latent image was discovered by Daguerre, who at first employed a silver plate coated with the iodide, development being effected by exposing the plate to the action of mercury-vapour. Later, he substituted glass for silver, and developed with a mixture of silver nitrate and ferrous sulphate. His discovery led to the introduction of the wet collodion process with silver iodide as the sensitive material.

Silver hypochlorite, AgOCl —A very unstable solution of the hypochlorite is formed by the action of chlorine-water on excess of silver monoxide. It soon decomposes into silver chloride and chlorate.

Silver chlorite, AgClO_2 —Silver nitrate and potassium chlorite react to form yellow crystals of the chlorite, an unstable substance decomposing energetically at 105° C.

Silver chlorate, AgClO_3 —The chlorate can be prepared by dissolving the monoxide in chloric acid, or by passing chlorine through a suspension of the monoxide in water, the hypochlorite being an intermediate product. It forms tetragonal crystals, melting at 230° C., and decomposing at 270° C. into silver chloride and oxygen. At ordinary temperatures its solubility is 20 grains per 100 grams of water.¹³ Its solution in ammonium hydroxide yields prismatic crystals, $\text{Ag}(\text{NH}_3)_2\text{ClO}_3$, melting at 100° C.

¹ Thomsen *Thermochimistry* (Longmans 1908) 284.

Berthelot *Ann Chém Phys* 1883 [5] 29 241.

² Jones and Hartmann *J Amer Chém Soc* 1915 37 752.

³ Brügel und Koef *Zeitsch anorg Chém* 1911 87 175 compare Taylor and Anderson *J Amer Chém Soc* 1921 43 2014.

Gerth *Zeitsch Pflztechn*, 1921 27 287.

⁴ Fischer *ibid* 1912 18 283 *Zeitsch anorg Chém* 1912 78 41.

⁵ Hellwig *Zeitsch anorg Chém* 1900 25 183 Berthelot *Compt rend*, 1880, 91, 1024 compare Klym *J Russ Phys Chém Soc* 1909 41 382.

⁶ Ihel *Zeitsch anorg Chém*, 1900 24 32.

⁷ Steger *Zeitsch physikal Chém* 1903 43 595.

⁸ Marsh and Rhymes *Trans Chém Soc* 1913 103 781.

⁹ Biltz and Stollenwerk *Zeitsch anorg Chém* 1920 114 174.

¹⁰ Hartung, *Trans Chém Soc*, 1922 121, 682 compare Koch and Schräder, *Zeitsch Physik*, 1921, 6 127.

¹¹ Wachter, *J prakt Chém*, 1843, 30, 330.

insinuate that the results in the above table are derived from inaccurate experiments In the course of my investigations, I have had to repeat the experiments of many , but have found no results to which my own in general approximated so nearly as to those of Mr Davy in his Researches As knowledge advances, however, greater precision is attainable from the same facts As for Mr Cavendish's important experiments, they were intended to shew what elements constitute nitric acid, rather than the proportion of them , and they were made at too early a period of pneumatic chemistry to obtain precision

The first line of the table contains the proportions of azote and oxygen in nitrous gas, as determined by the combustion of pyrophorus Mr Davy justly considers this as least entitled to confidence The second and third were obtained from the combustion of charcoal in nitrous gas The second is grounded upon the oxygen found in the carbonic acid By making the calculation of this from more recently determined proportions of charcoal and oxygen, I reduce the azote to 5 4 The third is derived from the azote left after combustion Mr Davy finds 15 4 measures of nitrous gas yield 7 4 of azote , or 10' measures of nitrous gas yield 48 measures of azotic g is

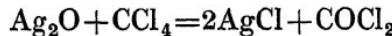
formula Ag_4O ¹. It is also said to be produced by reduction of silver monoxide by hydrogen at 88° C,² and by other methods³

Silver monoxide, Ag_2O —Addition of the hydroxide of barium or of an alkali-metal to silver nitrate solution precipitates the monoxide as a blackish, amorphous powder, which crystallizes from ammoniacal solution in violet crystals. Its density is given as 7.148 and 7.250. Ammoniacal silver oxide has been known to explode, the phenomenon being probably due to the formation of "fulminating silver" (compare p. 315).⁴

The monoxide is decomposed by heat into silver and oxygen, the liberated metal playing the part of an autocatalyst in accelerating the reaction.⁵ Finely divided platinum and manganese dioxide also cause acceleration of the transformation. It is decomposed by the action of light, with evolution of oxygen, and possibly formation of silver suboxide.

Silver monoxide dissolves in water, forming an alkaline solution which turns red litmus blue. At 25° C its solubility corresponds with 2.16×10^{-4} gram-molecule per litre of water,⁶ and at 15° C Rebière⁷ found the same value. It is a strong base, its salts having a neutral reaction. The solution is coloured reddish and decomposed by the action of light, the change being possibly attended by deposition of the suboxide or of colloidal silver.

Its heat of formation is about 6.4 Cal.⁸ It decomposes hydrogen peroxide, with liberation of metallic silver.⁹ With carbon tetrachloride it reacts at 250° C in accordance with the equation¹⁰



In the moist condition it finds extensive application in organic chemistry to the replacement of halogen by hydroxyl.¹¹ It can act as a reducer.¹²

Argentic oxide, AgO —A hot alkaline solution of potassium permanganate partially oxidizes silver monoxide to argentic oxide.¹³



The reaction is reversible. This oxide is said to be formed by anodic oxidation of silver in alkaline solution.¹⁴ It is a weaker base than the monoxide, but its solution in concentrated nitric acid contains $\text{Ag}(\text{NO}_3)_2$. Barbier regards it as belonging to the class of ozonides, and differing

¹ Guntz *Compt. rend.* 1891 112 861

Classen *Zeitsch. anorg. Chem.* 1903 36 9

² Wohler *Annalen* 1857 101 363 1860 114 119 Rose *Pogg. Annalen* 1852 304 Muthmann *Ber.* 1887 20 983 von der Pforder *ibid.* 1407 Leduc and Labrouste *Compt. rend.* 1907 145 55

³ Maignion *Bull. Soc. chim.* 1908 [4] 3 618

⁵ Lewis *Zeitsch. physikal. Chem.* 1905 52 310

⁶ Noyes and Kohl *ibid.* 1903 42 336

⁷ Rebière *Bull. Soc. chim.* 1915 [4] 17 309

⁸ Lewis *Zeitsch. physikal. Chem.* 1906 55 449 compare Thomsen *Thermochimistry* (Longmans 1908) 284 Perthelet *Compt. rend.* 1878 87 575 667 *Ann. Chim. Phys.* 1878 [5] 15 186

⁹ Compare von Breyer and Villiger *Ber.* 1901 34 749 2769

¹⁰ Michael and Murphy *Trans. Chem. J.* 1910 44 365

¹¹ Compare Madsen *Zeitsch. anorg. Chem.* 1912 79 195

¹² Chandrasena and Ingold *Trans. Chem. Soc.* 1922, 121, 1552

¹³ Barbier *Atti R. Accad. Lincei* 1907 [5] 16 II 72

¹⁴ Luther and Pokorný *Zeitsch. anorg. Chem.* 1908, 57, 290 compare Baboiovsky and Kuzma, *Zeitsch. Elektrochem.* 1908, 14, 196

great importance It not only shews the constitution of nitrous gas, but that of nitric acid also It appears, that by electrification exactly *one half* of the azotic gas is liberated, and its oxygen joins to the *other half* to form nitric acid The immediate effect of the electric shock is to separate the atoms of azote and oxygen, which by their junction form nitrous gas , the moment the oxygen is liberated, it is seized by another atom of nitrous gas, and the two united form an atom of nitric acid which escapes into the water In other words, 100 measures of nitrous gas contain 48 of azote , by electrification, 24 measures of azote are liberated, and the other 24 measures acquire the oxygen lost by the former, and become nitric acid, which are absorbed by the water

A repetition of Mr Cavendish's experiments will be found to confirm the above conclusion I have in three or four instances undertaken experiments of the same nature, and with like results , but as these are of a laborious kind, it is not so convenient to execute them One of these was more particularly an object of attention, and I shall relate it in the detail A quantity of pure oxyogenous gas was diluted with common air by degrees till the mixture contained 29 measures per cent of azote, that

sponding with 1.2×10^{-16} gram atom of silver per litre¹. When heated with silver sulphate at 300°C , both salts are reduced to metallic silver². In the fused state it is miscible with molten silver in all proportions. When heated in vacuum, it decomposes into its elements rapidly at 810°C ³.

The interaction of silver sulphide and mercury is considered on p. 290, and that with cyanides on p. 292.

Silver sulphite, Ag_2SO_3 —The sulphite is prepared by precipitating silver nitrate with the theoretical proportion of sulphurous acid or sodium sulphite, the salt being decomposed by excess of the acid, and dissolved by excess of the sulphite. It is a white substance, its colour changing under the influence of light to purple and then to black. Its solubility⁴ in water is less than 1/20000. When boiled with water, it decomposes in accordance with the equation



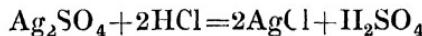
When heated alone, 10 per cent decomposes as indicated, and the remainder is converted into silver dithionate and metallic silver⁵



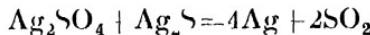
Several complex sulphites of silver with sodium and ammonium have been described⁶.

Silver sulphate, Ag_2SO_4 —The sulphate is produced by dissolving the metal in sulphuric acid, and by the action of this acid on the nitrate⁷. It forms white, rhombic crystals, isomorphous with those of the corresponding sodium salt, and melting at low red heat. Its density is 5.45⁸. The solubility of silver sulphate in water at various temperatures has been only partially investigated. At 14.5°C , 100 grams of saturated solution contain 0.730 gram of silver sulphate⁹, at 25°C the solubility is 0.0267 gram-molecule per litre of water¹⁰. Its heat of formation from the metal, oxygen, and sulphur dioxide is 96.20 Cal¹¹.

When the sulphate is heated to fusion in a current of hydrogen chloride, it is converted completely into chloride¹².



Heating with silver sulphide causes partial reduction to metallic silver¹³.



From the solution in dilute sulphuric acid three acid salts have been obtained— AgHSO_4 , pale yellow prisms, $2\text{Ag}_2\text{O}, 5\text{SO}_3, 5\text{H}_2\text{O}$, lustrous

¹ Bodlender and Lucas *Zeitsch. anorg. Chem.*, 1904, 41, 192.

Sackur *Ber.* 1908, 41, 336.

² Dumm and Meiss *Ber.* 1907, 40, 4775.

³ Baubigny *Compt. rend.* 1909, 149, 858.

Baubigny *ibid.* 735, 858.

⁴ Svensson *Ber.* 1871, 4, 713. Rosenheim and Steinhausen *Zeitsch. anorg. Chem.*, 1900, 25, 72.

⁵ Compte des Bull. Acad. roy. Belg. 1860 [2], 9, 322.

⁶ Richards and Jones *Zeitsch. anorg. Chem.* 1907, 55, 72.

⁷ Barré *Ann. Chim. Phys.* 1911, [8], 24, 145.

⁸ Rothmund *Zeitsch. physikal. Chem.* 1909, 69, 523.

⁹ Thomsen *Thermochemistry* (Longmans 1908), 323.

¹⁰ Richards and Jones *loc. cit.*

¹¹ Sackur *Abegg and Auerbach's Handbuch der anorg. Chem.*, Leipzig 1908, 2, 1, 714.

experiments The first line shews the results derived from the combustion of hydrogen in nitrous oxide From several experiments, Mr Davy selects one in which 39 measures of nitrous oxide and 40 of hydrogen were fired together, and seemed just to saturate each other, leaving a residuum of 41 azote , but this residuum must have contained a few atoms of azote originally mixed with the oxide and the hydrogen, and may therefore be supposed to be overrated If we suppose 39 oxide to contain 40 azote, it will reduce the weight of an atom of azote from 6 1 to 5 6 In my own experience, equal volumes of nitrous oxide and hydrogen, saturate each other, and the volume of azote left is equal to one of the other two, making the due allowance for impurities This would imply that a measure of azote + half a measure of oxygen, should, when combined, constitute a measure of nitrous oxide , but the united weights are about 5 per cent too little, according to the specific gravity of the oxide given above I apprehend the oxygen this way is underrated, owing perhaps to the formation of an unperceived quantity of nitric acid In the second line, we have the proportions of azote and oxygen in nitrous oxide, derived from the combustion of both phosphuretted hydrogen and charcoal

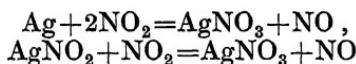
and is exploded energetically by percussion or by exposure to green light. It is suitable for use as a general primer¹

Berthollet's "fulminating silver" is produced by addition of alcohol to a concentrated solution of silver monoxide in ammonium hydroxide. It forms small, black crystals, exploded by friction, and soluble in potassium-cyanide solution. It probably has the formula NAG_3 or NAgH_2 ,² and it has no connexion with silver fulminate, CNOAg .

Silver hyponitrite, $\text{Ag}_2\text{N}_2\text{O}_2$ —Addition of silver nitrate to solutions of alkali-metal hyponitrites produces the hyponitrite as a yellowish precipitate. It is very slightly soluble in water, is sensitive to light and is decomposed by heat into silver, nitrogen oxides, and nitrogen.³

Silver nitrite, AgNO_2 —Sodium nitrite⁴ and the corresponding salts of potassium and barium react with silver nitrate to form silver nitrite. It crystallizes in long, greenish yellow, rhombic needles, the density at 0° C being 4.542, and between 21° and 31° C 4.453.⁵ At 15° C its percentage-solubility is 0.2752,⁶ and at 18° C 0.0216 gram-molecules dissolve in 1 litre of water.⁷

In the moist condition the salt is readily reduced by organic matter.⁸ When heated rapidly *in vacuo*, it is completely decomposed into silver and nitrogen peroxide. Slower heating in air causes side reactions in accordance with the equations⁹



Several double salts with alkali-metal nitrites have been described.¹⁰ Double compounds with ammonia of the formulae $\text{AgNO}_2 \cdot \text{NH}_3$, $\text{AgNO}_2 \cdot 2\text{NH}_3$, and $\text{AgNO}_2 \cdot 3\text{NH}_3$ have also been prepared.¹¹ A double salt with caesium, $\text{AgCs}(\text{NO}_2)_2$, is formed by the interaction of caesium nitrite and silver nitrite. It crystallizes in lemon yellow needles.¹²

Silver nitrate, AgNO_3 —Silver, silver monoxide, silver sulphide, and silver carbonate dissolve in nitric acid. Concentration of the solutions yields colourless, rhombic crystals of silver nitrate, of melting-point 208.6° C., and density 4.3554. It is characterized by its caustic action on the skin, its power of blackening it, its antiseptic properties, and its metallic taste.

¹ Wöhler and Matter, *Zeitsch. ges. Schuss und Sprengstoffwesen* 1907, 2, 181, 203, 244, 265.

² Kischner, *Annalen* 1886, 233, 93; compare Sieverts, *Zeitsch. angew. Chem.* 1909,

²² 6

³ Kirschner, *Zeitsch. anorg. Chem.* 1898, 16, 424; Hantzsch and Kaufmann, *Annalen* 1896, 292, 317; Divers, *Trans. Chem. Soc.* 1899, 75, 108; *Proc. Chem. Soc.* 1907, 23, 266; Angeli and Marchetti, *Ital. R. Accad. Naz. Lincei* 1908, [5], 17, 1, 695; Ray and Ganguli, *Trans. Chem. Soc.* 1907, 99, 1402.

⁴ Oswald, *Inn. Chem. Phys.* 1914, [9], 1, 32.

⁵ Ray, *Trans. Chem. Soc.* 1908, 93, 997.

⁶ Creighton and Ward, *J. Amer. Chem. Soc.* 1915, 37, 2333.

⁷ Abegg and Pick, *Ber.* 1905, 38, 2571; *Zeitsch. Elektrochem.*, 1906, 12, 592; *Zeitsch. anorg. Chem.* 1905, 51, 1.

⁸ Oswald, *loc. cit.*

⁹ Oswald, *Compt. rend.* 1911, 152, 381; compare Abegg and Pick, *Ber.* 1905, 38, 2571; *Zeitsch. Elektrochem.* 1906, 12, 592; *Zeitsch. anorg. Chem.*, 1906, 51, 1.

¹⁰ Kischner, *Pogg. Annalen* 1878, 74, 120.

¹¹ Reichert, *Ber.* 1883, 16, 2425.

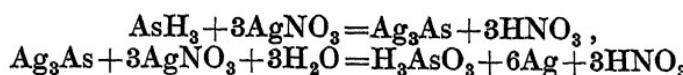
¹² Jamieson, *Amer. Chem. J.*, 1907, 38, 614.

weight of an atom of azote will be accordingly found = 5 25

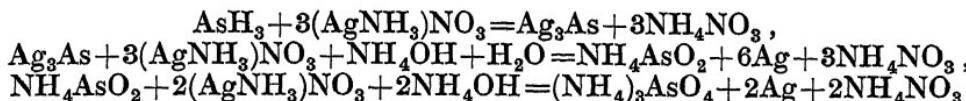
It is remarkable, that in the combustion of hydrogen in nitrous oxide, the oxygen (as estimated by the loss of hydrogen) is usually found below par, and it is the same with the azote in the combustion of olefiant gas, as Mr Davy has remarked, I have found it so likewise with carburetted hydrogen or coal gas I apprehend when azote disappears, it is from the formation of ammonia

Besides the three compounds of azote and oxygen already considered, there are at least two more One is called *nitrous acid*, it is a compound of nitric acid and nitrous gas The other I call *oxynitric acid*, it is a compound of nitric acid and oxygen Priestley discovered the fact that nitric acid absorbs nitrous gas very largely, and thereby becomes more volatile He found that 1²⁰ ounce measures of nitrous gas over water disappeared in a day or two, when a phial containing 96 water grain measures of strong nitric acid was inclosed with the gas The colour of the acid as it absorbs nitrous gas is gradually changed from pale yellow to orange, green, and finally blue green Mr Davy has used his endeavour to find the quantity of nitrous gas which nitri-

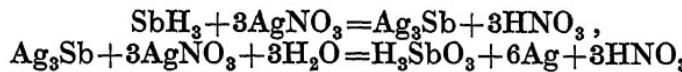
Arsine¹ reacts with a concentrated solution of silver nitrate, precipitating yellow $\text{Ag}_3\text{As} \cdot 3\text{AgNO}_3$, decomposed by water with liberation of metallic silver. With dilute silver nitrate the reaction occurs in two stages



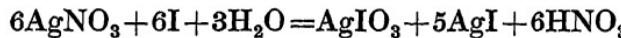
In presence of dilute ammonium hydroxide reduction to metallic silver takes place in three stages, ammonium arsenate and nitrate being simultaneously formed



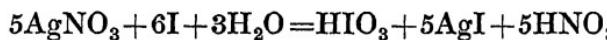
The action of stibine² is similar to that of arsine, but only about 2 per cent of the antimonious acid formed dissolves, the rest remaining in the precipitate



Excess of silver nitrate reacts with iodine in accordance with the equation



When the iodine is in excess, the reaction is represented by the equation



The second reaction is applicable to iodometry, the titration of alkali metal hydroxides, and the titration of silver nitrate³

With mercury a solution of silver nitrate yields various amalgams and crystalline double compounds of silver and mercury⁴

Silver nitrate forms double salts with the halides, cyanide, and thiocyanate of silver⁵. It also yields with silver sulphide a compound containing equimolecular proportions of the two salts, prepared as a yellowish-green precipitate by the action of hydrogen sulphide on a concentrated solution of silver nitrate. It forms other double salts with the nitrates of lithium and sodium,⁶ potassium,⁷ ammonium,⁸ and thallium.⁹ The solution of silver nitrate in ammonium hydroxide yields rhombic prisms, $\text{AgNO}_3 \cdot 2\text{NH}_3$, isomorphous with silver nitrate.¹⁰

¹ Reckleben, Loeckmann and Fockhardt *Zeitsch anal Chem.* 1907 **46** 671. Reckleben and Loeckmann *ibid.* 1908 **47** 126.

Reckleben *Ber.* 1909 **42** 1458.

² Pawlow and Schem *J. Russ. Phys. Chem. Soc.* 1907 **39** 943.

³ Compare Reinders *Zeitsch physikal. Chem.* 1902 **42** 225; 1906 **54** 607, Ogg *ibid.* 1898 **27** 285.

Hellwig *Zeitsch anorg. Chem.* 1900 **25** 183. Jüger *Zeitsch Kryst. Min.* 1907 **44** 169. Scarpia *Atti R. Accad. Nazur.* 1913 [5] **22** II 452.

⁴ Hissink *Zeitsch physikal. Chem.* 1900 **32** 543.

⁵ Rutgers *ibid.* 1889 **4** 608. Schreinemakers *ibid.* 1909 **65** 553. Schreinemakers and de Bruat *Chem. Weekblad* 1910 **7** 259.

⁶ Schreinemakers *loc. cit.* Schreinemakers and de Baat, *loc. cit.*

⁷ van Fyck, *Proc. K. Akad. Wetensch. Amsterdam* 1900 **2** 543.

⁸ Reichler *J. Chim. phys.* 1903 **1** 345. compare Castoro *Gazzetta* 1907 **37** 1.

⁹ Hantzsch, *Zeitsch anorg. Chem.*, 1899 **19** 104.

ceased, which will be half a minute, the residuary gas is transferred into another tube, it will be found that 1 measure of oxygen and 1 8 of nitrous gas have disappeared, the mixture is to be made over water

2 When 4 measures of oxygen are put to 1 3 of nitrous gas in a tube two tenths of an inch in diameter, and 10 inches long, so as to fill it, it will be found that 1 measure of oxygen will combine with 1 3 of nitrous gas, in 4 or 5 minutes

3 When 1 measure of oxygen and 5 of nitrous gas are mixed together, so as to form a thin stratum of air, not more than $\frac{1}{8}$ th of an inch in depth (as in a common tumbler), it will be found that the oxygen will take from 3 to $3\frac{1}{2}$ measures of nitrous gas in a moment, and without any agitation If equal measures are mixed, then 1 oxygen takes about 2 2 nitrous

4 When water has been made to imbibe a given portion of oxygenous gas, and is afterwards agitated in nitrous gas, the quantity of nitrous gas absorbed will always be more than exhausted water would take, by a quantity equal to 3 4 or 3 6 times the bulk of the oxygenous gas And, *vice versa*, when water has imbibed a portion of nitrous gas, and is then agitated with oxygenous gas the quantity

in solid solution. Addition of silver arsenate to an aqueous solution of arsenic acid precipitates a white, crystalline compound, $\text{Ag}_2\text{O} \cdot 2\text{As}_2\text{O}_5$, decomposed by water into silver arsenate and arsenic acid¹.

Silver carbide, Ag_2C_2 —Excess of an aqueous solution of acetylene precipitates from ammoniacal silver nitrate the greyish-yellow carbide. On exposure to light it darkens rapidly. When heated, the dry salt explodes. With hydrochloric acid it evolves acetylene, and with nitric acid it undergoes complete decomposition. Water causes hydrolysis to some extent, with production of silver monoxide. Agitation with sodium-chloride solution causes similar hydrolysis, the solution becoming strongly alkaline². The heat of formation from the elements is given by Berthelot as —87.15 Cal. It forms a series of double salts with the halides, sulphate, and nitrate of silver³.

Silver carbonate, Ag_2CO_3 —When the equivalent proportion of potassium carbonate or potassium hydrogen carbonate is added to a solution of silver nitrate, silver carbonate is precipitated as a yellow powder. Addition of excess of potassium carbonate causes simultaneous precipitation of a proportion of silver monoxide. Pure silver carbonate is white, but is sensitive to light. At 200° C it decomposes with evolution of carbon dioxide⁴. Its heat of formation is 120.8 Cal⁵. Silver nitrate precipitates from a hot, concentrated solution of potassium carbonate a double salt of the formula $\text{Ag}_2\text{CO}_3 \cdot \text{K}_2\text{CO}_3$. A crystalline double compound with ammonia of the formula $\text{Ag}_2\text{CO}_3 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ is produced by the spontaneous evaporation in air of an ammoniacal solution of silver oxide. Under the influence of sunlight the crystals become black, and on exposure to air they lose water and ammonia, yielding silver carbonate⁶.

Silver cyanide, AgCN —A white, amorphous precipitate of the cyanide is obtained by interaction of a silver salt and a cyanide in aqueous solution. It crystallizes from a hot concentrated solution of potassium carbonate in fine needles. It is unaffected by light, but heat eliminates one-half of the cyanogen with production of silver "paracyanide"⁷. Both hydrochloric acid and mercuric chloride convert it into silver chloride. With hydrogen sulphide it yields silver sulphide, and heating with sulphur transforms it into silver thiocyanate. Its heat of formation from silver and cyanogen is 3.6 Cal⁸. There is some evidence of the existence of silver cyanide in two polymeric forms, AgCN and $\text{Ag}_2(\text{CN})_2$. With hydrazine cyanide it forms colourless crystals, $\text{AgCN} \cdot \text{N}_2\text{H}_4$, which blacken in contact with air¹⁰.

Solution of silver or its cyanide in potassium cyanide forms potassium silver cyanide, $\text{KAg}(\text{CN})$, octahedral crystals stable in air, but blackened by light. At 20° C its solubility is 25 grams per 100 grams of water¹¹.

¹ Hartzig und Gauthier *Annalen* 1859 **III** 168.

Bredig und Usoff *Zeitsch. Elektrochem.* 1896 **3** 116.

² Compire Berthelot *Compt. rend.* 1890 **129** 361; Losen *Annalen* 1893 **272** 139.

Kiesel Amer. J. Sci. 1902 [1] 14 285; Ellington *Chem. News* 1892 **65** 295.

³ Joulin *Ann. Chim. Phys.* 1873 [1] 30 260.

Colson *Compt. rend.* 1909 **148** 837.

⁴ Drivin and Olmer *ibid.* 1921 **172** 1662.

⁵ Rummelsberg *Jogg Annalen* 1848 **73** 80.

⁶ Berthelot *Ann. Chim. Phys.* 1883 [5] **29** 241.

⁷ Wagner *Vork. Ges. deut. Naturforsch. Aerzte* 1902 **1** 69.

⁸ Fianzen and Fuelling *Zeitsch. anorg. Chem.* 1911 **70** 145.

⁹ Baup *Ann. Chim. Phys.* 1858 [3] **53** 464.

accord'g to circumstances takes any intermediate portion? Are there indefinite gradations in the compound? I cannot conceive this, neither do the facts at all require it All the products that need be admitted to explain the facts are three It has been shewn that 1 measure of oxygen requires 1 8 of nitrous gas to form nitric acid, according to the results derived from the electrification of nitrous gas, and the conclusion is corroborated by other facts It appears from the above observations 3 and 4, that oxygen is found sometimes to combine with 3 6 times its bulk of nitrous gas, and that this is the maximum, but it is just twice the quantity requisite to form nitric acid it is evident, therefore, that a compound is formed in which there are twice as many atoms of nitrous gas as are necessary to form nitric acid This then may be called *nitrous* acid, and the elementary atoms consist of 1 of oxygen and 2 of nitrous gas, united by chemical affinity If the other extreme, or the minimum quantity of nitrous gas to which oxygen had united, had been 9, or half what is found in nitric acid, then this would have shewn the union of 2 atoms of oxygen with 1 of nitrous gas, and the compound might be called *orynitric* acid Now, though it does not appear that we are able as yet to form

The relative insolubility of some of the salts of silver is in the order *chloride, cyanide, thiocyanate, bromide, iodide, and sulphide*. The metal is usually estimated gravimetrically as chloride, or by electrolytic deposition. It can also be weighed as chromate¹. Other gravimetric methods are reduction to metal by hypophosphorous acid,² and by alkaline glycerol and other reagents.³

Volumetric estimation⁴ in neutral solution can be effected by titration with standard sodium chloride, potassium chromate being employed as indicator, and in nitric-acid solution with thiocyanate, using ferric alum as indicator, or with sodium chloride without any external indicator.

¹ Gooch and Bosworth, *Zeitsch anorg Chem*, 1909, 62, 69, 74

² Mawrow and Mollow, *ibid*, 1909, 61, 96

³ Whitby, *ibid*, 1910, 67, 62

⁴ Compare also Gooch and Bosworth, *loc cit*

1 Nitrous Gas

Nitrous gas is formed by pouring dilute nitric acid upon many of the metals, it should be received over water. The best mode of procuring it is to put a few small pieces or filings of copper into a gas bottle, and pour nitric acid of the specific gravity 1 2 or 1 3 on to them, the gas comes over in a state of purity (except so far as it is diluted with atmospheric air) and without the application of heat. The common explanation of this process is, that a part of the nitric acid is decomposed into the elements nitrous gas and oxygen, its oxygen unites to the metal to form an oxide, which the rest of the acid dissolves. Upon a more particular examination of the phenomena, I find, that estimating the quantity of real acid by Kirwan's table, $\frac{1}{3}$ part of the acid is decomposed to furnish oxygen to the metal, and to yield nitrous gas, $\frac{1}{3}$ unites to the metallic oxide, and the remaining $\frac{1}{3}$ seizes the nitrous gas, and forms nitrous acid, but in the degree of condensation of the acid, it is unable to hold more than $\frac{1}{3}$ or $\frac{1}{2}$ of it, and the rest is therefore evolved. For example, 200 grain measures of nitric acid of 1 32 strength, diluted with 100 water, dissolved 50 grains of

Norway The cyanide-process has been highly developed in South Africa, and the electrolytic separation from copper in America

History —Gold has been esteemed a precious metal from prehistoric times. The high value placed on it is indicated by the writings of Homer and of Biblical authors. The locality of the ancient sources of supply is now a matter of doubt, but there appear to have been extensive deposits, now probably worked out.

In the code of Menes, who was King of Egypt about 3600 B.C., the ratio in value between gold and silver is given as 1 part of gold to 25 parts of silver. Corresponding with the period about 2500 B.C. there are extant Egyptian rock carvings illustrating the washing of auriferous sands and the subsequent smelting. The sands were washed over smooth, sloping rocks by running water, and the gold was caught in the hair of raw hides spread on rocks. The "Legend of the Golden Fleece" probably originated in the use of sheepskins for this purpose. It narrates the story of a piratical expedition made about 1200 B.C. with the object of stealing gold obtained from rivers by the aid of sheep or goat skins in the region now termed Armenia.

Chikashige¹ found gold associated with other metals in a Buddhist statue of the third century A.D., and also in a Corcan bronze mirror of the tenth century A.D.

The word "gold" is probably derived from the Sanskrit *Jvalita*, from *Jval*, meaning to shine.²

Gold coins were first made in the Western world about 700 B.C. The pairing of gold and silver was then practised, ancient Greek coins containing 99.7 to 99.8 per cent of gold. The process was one of cementation. At a later period pairing was accomplished by means of nitric acid. At the present time the pairing of gold from silver is effected by chlorine in Australia, by electrolysis in America, and by sulphuric acid in Europe.³

Extraction⁴ There are four main processes of gold extraction:

- 1 Mechanical processes for preparing and washing the ore.
- 2 Preparation of the ores with simultaneous or subsequent amalgamation.
- 3 Chemical extraction processes.
- 4 Smelting of certain ores.

(1) WASHING PROCESSES

Gold can be extracted by washing only when it is present as metal in the form of particles which are not too minute. The washing removes the specifically lighter parts of the material, the heavier gold particles sinking to the bottom. The process is applicable directly to gold bearing sand and to gold bearing rocks after crushing. The crushing is effected by stone crushers, rolling mills and stamp mills. The washing is carried out either by subjecting the material to the prolonged

¹ Chikashige, *Trans. Chem. Soc.* 1920, 117, 917.

Compare Euse, *Metallurgy of Gold*, 6th ed. (Griffith, 1915), 2.

² Compare Sir T. Kirk Louse's Presidential Address to the Institute of Mining and Metallurgy, March 18, 1915, *Nature* 1915, 95, 100.

³ For full metallurgical details reference should be made to *The Metallurgy of Gold* by Sir T. Kirk Louse (Griffith) and *The Sampling and Assay of Precious Metals* by F. A. Smith (Griffith).

stantly fatal It extinguishes combustion in general , but pyrophorus spontaneously takes fire in it , and phosphorus and charcoal in an ignited state burn in it, and produce a decomposition Pure water, (that is, water free from all air) I find, absorbs about $\frac{1}{8}$ th of its bulk of nitrous gas , but only $\frac{1}{7}$ th of it can be expelled again by other gases it should seem, then, that a small portion of the gas actually combines with the water, while the greater part is, like most other gases, mechanically retained by external pressure

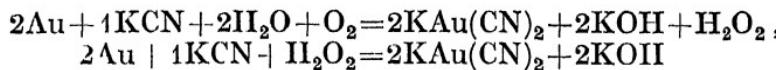
Nitrous gas, as has been observed, is decomposed by electricity one half of the azote is liberated, and the other half unites with the evolved oxygen, and forms nitric acid According to Davy's analysis by charcoal, nitrous gas is constituted of 22 azote, and 3 oxygen by weight , or 42 azote, and 58 oxygen per cent nearly , which is the same as I obtain by electricity and other means If completely decomposed, 100 measures would be expanded to 104 6, of which 48 would be azote, and 56 6 oxygen

Dr Henry has recently discovered that nitrous gas is decomposed by ammoniacal gas , the two gases are mixed over mercury in Volta's eudiometer, and an electric spark is found sufficient to explode them When an

alkali. The residue is extracted with 0.35 per cent solution of potassium cyanide, then with 0.08 per cent solution, and ultimately with water. The extract is transferred to tanks, and the gold precipitated as a powder by addition of zinc. It is then washed out from the bottom of the tanks, dried, and freed from zinc by roasting and fusing.

In the electrolytic precipitation of the gold an iron anode and a sheet-lead cathode are employed, the current density being very low, about 0.5 amp per sq mètre.¹ The gold is deposited on the lead, and after removal of this metal still contains a considerable proportion of both lead and silver. It is freed from them by the operation called "parting".

Access of air is essential to solution of gold in potassium cyanide,² the process being attended by evolution of hydrogen. Lead, bismuth, antimony, cadmium, silver, and mercury also dissolve in presence of air, but copper, iron, aluminium, nickel, cobalt, and zinc dissolve in absence of air. Gold and silver are distinguished by the fact that their maximum solubility corresponds with a very low concentration of the potassium-cyanide solution, a phenomenon probably due to the slight solubility of air in concentrated solutions of this salt.³ The solution of gold in the cyanide solution is accompanied by the intermediate formation of hydrogen peroxide, and the process is accelerated by addition of this substance.⁴



A similar accelerating effect is excited by other substances, such as potassium ferricyanide, potassium permanganate, potassium chromate,⁵ sodium peroxide,⁶ barium peroxide,⁷ cyanogen bromide,⁸ cyanogen chloride,⁹ persulphates and certain organic compounds.¹⁰ The best method of reducing the proportion of the other metals is to maintain the cyanide solution dilute.

In precipitating the gold by zinc, the proportion required is about seven times that indicated by the equation



the discrepancy being due to solution of part of the zinc in the cyanide solution with evolution of hydrogen.¹¹ Purity of the zinc is an important factor in counteracting this loss.

In the electrolytic deposition of gold from cyanide solutions hydrogen is liberated at the cathode and an equivalent number of hydroxyl ions give up their charges at the anode, the solution developing in alkaline reaction. Cyanogen ions also give up their charges at the anode, being

¹ Siemens, *Zeitsch. Elektrochem.* 1895, 2, 532.

Watts and Whipple, *Trans. Amer. Electrochem. Soc.* 1917, 32, 257.

² MacLennan, *Chem. News* 1893, 67, 191, 189, 71, 73.

³ Fodlender, *Ztsch. angew. Chem.* 1896, 19, 583.

Moldenhauer, *Ber.* 1893, 26, 340.

⁴ Montgomerie, *J. Soc. Chem. Ind.* 1893, 12, 767.

⁵ Schulz, *Mining J.* 1902, March 1.

⁶ Sulmann und Leed, *German Patent No. 83292*. Mullholland, *Berg. und Hüttenmännische Zeit.* 1896, 55, 66. Louis, *J. Soc. Chem. Ind.* 1899, 18, 229.

⁷ Morgan, *British Patent No. 18279*.

⁸ Schelin, *Zeitsch. Elektrochem.* 1896, 2, 507.

⁹ Uslar and Brilwein, *Cyanidproesse zur Goldgewinnung*, Halle 1903.

1 grain of the salt , its specific gravity was 1 081 , this was agitated with iron filings, to reduce any of the red sulphate that might be in the solution, which is known not to absorb the gas, into green sulphate A eudiometer was filled with mercury, except one measure, which was filled with the liquid solution , the tube was then inverted over mercury, and nitrous gas sent up to the solution, which was afterwards agitated It was repeatedly found that 1 measure of the solution absorbed 6 measures of the gas, and was then saturated Consequently 1500 grain measures of the solution would have taken 9000 grain measures of the gas , but 1500 of the solution contained 250 of salt, of which $\frac{1}{5}$ th was iron, as is well known , and 9000 grain measures of the gas weigh 12 grains Here, then, 50 grains of iron united to 12 grains of nitrous gas Now, the weight of an atom of iron is 50 (page 258), and that of nitrous gas is 12 It therefore follows, that in the combination of green sulphate of iron with nitrous gas, each atom of iron unites with an atom of the g ' , O_2 fully to the general law of chemical union

Nitrous gas is still used in eudiometry to determine the quantity of oxygenuous gas in any mixture , and on account of the ease and elegance of its application and the quickness

can be recovered only by a cumbrous process¹. To obviate this difficulty the metal, either after parting from silver or in its original state, is dissolved, and the gold and platinum precipitated separately.

Parting by aqua regia is effected by dissolving the alloyed gold in the acid, silver being converted into its chloride, which is then precipitated by dilution with water. The platinum dissolves completely, and the iridium partially, the gold being precipitated by addition of ferrous sulphate or chloride. With a large proportion of silver some of the gold is occluded, and escapes solution in the acid, thus necessitating a repetition of the treatment with acid. The process lacks many of the advantages characteristic of the electrolytic method.

The *electrolytic process*² was introduced in 1863 by Charles Watt at Sydney, started in 1878 by Wohlwill at Hamburg, and in 1902 by Tuttle at the Philadelphia Mint. In the gold chloride method the electrolyte is a solution of auric chloride containing free hydrochloric acid, the crude metal forming the anode, and pure sheet gold the cathode. The gold dissolved at the anode is deposited in a pure condition at the cathode. Other metals are converted into chlorides at the anode, and either remain dissolved or pass into the anodic slime. Silver is converted into its chloride, this substance partly dissolving, partly depositing in the slime, and partly adhering to the anode. With solutions containing more than 3 to 10 per cent of hydrochloric acid, and with bullion having more than 6 per cent of silver, the coating of the anode raises the density of the current and causes evolution of chlorine.

Rose has found that with an electrolyte containing 29 per cent of free hydrochloric acid and with a current density of 5000 amperes per square metre of anode surface no chlorine is evolved, even with an anode containing 20 per cent of silver. The heavy current causes the silver chloride to separate from the anode, and as aurous chloride is not allowed to form deposition of gold in the anode slime is prevented.

A solution of auric chloride containing 3 to 5 per cent of gold and a current density of 1000 amperes per square metre are usually employed, but Rose has found that with a current density of 5000 amperes per square metre in electrolyte with 20 per cent of gold yields a coherent deposit capable of being readily washed and malleable after melting. By this modification the time required for solution of the anode is reduced from one week to one day.

In addition to the malleable nature of the product obtained by electrolytic refining the process also extracts platinum, a constituent of nearly all samples of Transvaal gold. The United States of America Mint has found the electrolytic method more economical than that with sulphuric acid.

Miller's *dry parting process*³ involves the action of chlorine on molten gold covered with a layer of borax to prevent sputtering. The gold is not attacked but the silver is converted into chloride. When the gold has solidified the molten silver chloride collected on the surface is run off, carrying with it a small proportion of gold. When silver is the chief

¹ Petten ofer *Dingler's Polytech J* 1817 104 118 195.

Compare Wohlwill *Ztsch Elektrochem* 1898 4 379 421. See E. K. Rose Presidential Address to the Institute of Mining and Metallurgy March 18 1915 *Nature* 1915 95 100.

² Miller *J pratt Chem* 1869 106 503. *Dingler's Polytech J* 1868 188, 251 1870 197 43 1872 205 535 1873 208 342.

rious proportions, according as one or other is in excess. Sometimes 3 measures of nitrous are saturated with 2 of the acid, and sometimes with 4 measures. When green sulphate of iron is saturated with a known portion of nitrous gas, and the solution is afterwards agitated with oxygen, the absorption is somewhat slow, (like that with sulphuret of lime) and the quantity taken up is equal in bulk to the nitrous gas. The liquid, from a dark red or black, becomes of a bright yellowish red, the oxide of iron being changed from the green to the red during the process.

It has been made appear, that by electricity *one half* of the atoms of nitrous gas are decomposed, in order to oxygenize the other half, in like manner, in certain cases, *one half* of the atoms of nitrous gas are decomposed to *azotize* the other half. This is shewn by the experiments of Priestley, but much more accurately by those of Davy. The alkaline sulphites, muriate of tin, and dry sulphures, convert nitrous gas into nitrous oxide. According to Davy, 16 cubic inches of nitrous gas were converted into 7 8 of nitrous oxide by sulphite of potash, that is, 100 measures gave 48 75. He also found, that muriate of tin and dry sulphures changed 100 measures of nitrous gas into nitrous oxide. These bodies have

Cassius as a mixture of colloidal gold and colloidal stannic acid, a view practically identical with that of Debray expressed in modern phraseology¹

Physical Properties — Gold is a metal of characteristic yellow colour. Its melting-point is given as 1035° C,² 1037° C,³ 1059.3° C,⁴ 1061.7° C,⁵ 1062.4° C,⁶ 1063° C,⁷ 1063.9° C,⁸ 1064° C,⁹ 1071° C,¹⁰ and 1072° C.¹¹ The most probable value is about 1063° C. Capua¹² found that the presence of between 6 and 7 per cent of silicon lowers the melting-point about 800° C. Its boiling-point was determined by Moissan¹³ with the aid of the electric furnace to be about 2530° C, being higher than that of copper and lime. Its density is given as 19.21,¹⁴ 19.2685,¹⁵ 19.28,¹⁶ 19.43,¹⁷ that for unpressed gold being 18.884.¹⁸ The approximate value may be taken as 19.3. The specific heat at low temperatures is given as 0.0297,¹⁹ as 0.0302 at 0° C,²⁰ as 0.0380 at 18° C,²¹ and as 0.0324²² and 0.0316²³ at 0° to 100° C. The latent heat of fusion per gram is 0.0163 Cal.²⁴ The hardness on Auerbach's scale is 2.5 to 3.²⁵ Gold is the most malleable of the metals, and can be beaten out to leaves 0.0001 mm thick.²⁶ One gram of the metal can be drawn out to a wire 166 mètres in length. Thin layers deposited on glass by heating *in vacuo* are almost colourless in reflected light, but appear of a rose to violet colour by transmitted light.²⁷ Neither hydrogen nor nitrogen is absorbed by gold, either in the solid or fused state.²⁸ It is a good conductor of both heat and electricity.

Chemical Properties — The chemical character of the metal accords with its low electroaffinity, an example being its stability towards the action of strong acids, although boiling, concentrated nitric acid dissolves

¹ Compare Schneider *Zeitsch. anorg. Chem.* 1893, 5, 80; Grunwald *Sprechsaal* 1910

43 419

Violle *Compt. rend.* 1879, 89, 702

² Bequerel *ibid.* 1863, 57, 955

³ Day and Clement *Amor. J. Sci.* 1908 [4], 26, 105

Hegel and Neville *Trans. Chem. Soc.* 1895, 67, 1021

⁴ Day and Sosman *Amor. J. Sci.* 1910 [1], 29, 93

⁵ Guerlitz and Pfeiffer *Zeitsch. Metallkunde* 1919, II, 1; Dunn and Foote *Trans. Faraday Soc.* 1920, 15, 186

⁶ Holborn and Day *Philos. Annalen* 1901, 4, 99

⁷ Lethelot *Compt. rend.* 1898, 126, 173

⁸ Ruff and Coecke *Zeitsch. anorg. Chem.* 1911, 24, 1159

⁹ Holborn and Wien *Philos. Annalen* 1892, 47, 107

¹⁰ Capua *Ital. Accad. Lincei* 1920, [5], 29, 1, 111

¹¹ Moissan *Compt. rend.* 1903, 141, 977; compare von Wartenberg, *Zeitsch. anorg. Chem.* 1908, 56, 320

¹² Weiss *Abhandl. Phys. Tech. Reichsanstalt* 1900, 3, 269

¹³ Kahlbaum und Foth *Zeitsch. anorg. Chem.* 1901, 29, 177

¹⁴ Voigt *Philos. Annalen* 1893, 49, 709

¹⁵ Averilloff *Zeitsch. anorg. Chem.* 1903, 35, 335

¹⁶ Kahlbaum und Foth *ibid.* 1901, 29, 177

¹⁷ Richards and Jackson *Zeitsch. physikal. Chem.* 1910, 70, 111; compare Nordmeyer *Ber. Deut. physik. Ges.* 1908, 6, 202

¹⁸ Schimpff *Zeitsch. physikal. Chem.* 1910, 71, 257

¹⁹ Weiss *Abhandl. Phys. Tech. Reichsanstalt* 1900, 3, 269

²⁰ Regnault *Ann. Chem. Phys.* 1840, [2], 73, 1

²¹ Violle *Compt. rend.* 1879, 89, 702

²² Compare Euler *Das Periodische System* Hamburg and Leipzig 1904, 115

²³ Lindolt *Formstein und Meyerhofer Tabellen* 3rd ed. Berlin 1905, 57

²⁴ Compare Muspratt *Handbuch der Technischen Chemie* Brunswick 1891, 3, 1829

²⁵ Houllier *Compt. rend.* 1909, 149, 1368

²⁶ Sieverts *Zeitsch. Elektrochem.* 1910, 16, 707

published an essay on the subject in the Journal de Physique for 1793, in which the constitution and properties of the gas were more fully investigated In 1800, Mr Davy published his Researches, containing a much more complete and accurate development of the nature of this gas, than had previously been given, as well as of the other compounds of azote and oxygen, and several other collateral ones

Nitrous oxide gas may be obtained from a salt called *nitrate of ammonia*, being a compound of nitric acid, ammonia and water The salt is put into a gas bottle, and heat applied, which first fuses the salt, about 300° , by continuing the heat, the fluid salt boils, and is decomposed about 400° , emitting nitrous oxide gas and steam, into which the whole of the salt is principally resolved The gas may be received either over water or mercury

The constitution of the salt, nitrate of ammonia, according to Davy, is when crystallized, 18 4 ammonia, and 81 6 acid and water Now, if we suppose an atom of ammonia to be constituted of one of azote, 5 1, and one of hydrogen, 1, as will be shewn hereafter and that an atom of the nitrate is composed of 1 atom of each of the elements, ammonia, nitric acid and water (see plate 4, fig 36),

Although derivatives of bivalent gold are known, there is no certainty as to the existence of an Au⁺ ion.

Applications—Alloys of gold with copper, silver, and other metals are employed in the manufacture of plate, jewellery, and coins. In the British coinage the metal is alloyed with copper, the coins containing 916 6 parts of gold per 1000. This alloy has a lower melting-point than gold, and is harder. In the United Kingdom there are five legal standards for gold wares, 22-carat (containing 22 parts of gold in 24), 18-carat, 15-carat, 12-carat, and 9 carat.

Gold leaf contains 90 to 98 per cent of gold alloyed with copper and silver. It is employed in gilding. Gold-plating is carried out in a bath of potassium auricyanide with a gold anode, the strength being maintained at about 6.85 grams of gold per litre by addition of auric chloride.

The metal finds application in photographic toning as sodium aurichloride. The chloride is employed in medicine, and in alloys in dentistry. "Purple of Cassius" is useful for colouring glass. *Gold lace* consists of a silk body with very fine strips of gold twined round the silk.¹

Atomic Weight—In the early years of the nineteenth century the subject of the ratio of gold to oxygen in gold oxide was investigated with divergent results by several chemists, including Richter, Prout, Oberkampf, Dalton, and Thomsen. Dalton² quoted the value of the atomic weight as being between 140 and 200 ($O=7$). In 1818 Berzelius² formulated aurous oxide as AuO , and auric oxide as AuO_3 , the corresponding atomic weight being $Au=2486$ ($O=100$) or 2×198.8 ($O=16$). This figure is about twice the modern value $Au=197.2$. In 1826 Berzelius was induced by a knowledge of the existence of oxides of the type R_2O_3 to assign to gold the atomic weight $Au=1243$ ($O=100$), corresponding with $Au=198.8$ ($O=16$) and to formulate the oxides of gold as Au_2O and Au_2O_3 . It was he substituted for these formulae the so-called "equivalent formula" written with letters having a central, horizontal stroke, Au^I and Au^{III} , corresponding with AuO and AuO_3 . He took 2158.3 as the equivalent and 1229.165 ($O=100$) as the atomic weight of gold.³ In 1817 Menecke gave the value $Au=200$, and in 1826 Gmelin gave as the equivalent $Au=66$. Later, the equivalent was assumed to be identical with the atomic weight $Au=196$ to 199 , the corresponding formula for the oxides being written as AuO and AuO_3 , and for the chlorides as $AuCl$ and $AuCl_3$.

The principal types of gold compounds are AuX and AuX_3 , those of the formula AuX being not improbably formed by combination of the other two forms. The atomic weight $Au=197.2$ is supported by cryoscopic and osmotic observations of solutions of gold in other metals indicating the monatomicity of the element. The vapour density of gold has not been determined nor that of any of its compounds. The atomic heat calculated from the specific heat and the atomic weight 197.2 has the normal value 6.4. The element is isomorphous with copper and silver. Its properties and those of its compounds are functions of the atomic weight 197 belonging to an element of the eleventh row of Group I or of the tenth row of Group VIII of the periodic system of Mendeleeff.

¹ For a bibliography of gold see Poole, *Metallurgy of Gold* 5th ed. (Griffin 1906). Berzelius, *K. Svenska Vet. Akad. Handl.* 1813, 185; *Schwed. S. J.* 1813, 7, 47.

² Berzelius, *Lehrbuch der Chemie* 5th ed. Dresden 1813-1818, 3, 1212.

more vigorously than in common air, it is unfit for respiration, but does not so immediately prove fatal as Dr. Priestley and the Dutch chemists concluded Mr Davy found that it may be respired for two or three minutes, and that it generally produces sensations analogous to those of intoxication It is absorbed by water to the amount of about 80 per cent according to my recent trials Davy makes it only 54 per cent, but he was not aware that the quantity is increased in proportion to the purity of the residuary gas Dr Henry finds from 78 to 86 per cent This gas of course expels other gases from water, and is itself driven off unchanged by heat It is a remarkable fact, that water should take so nearly, and yet not exactly, its bulk of this gas

Nitrous oxide, by long electrification, loses about 10 per cent of its bulk, some nitric acid is formed, and a mixture of azote and oxygen is found in the residuum, but no satisfactory decomposition is obtained this way

All the combustible gases, mixed with nitrous oxide, explode by an electric spark

Nitrous oxide can be made to combine with the fixed alkalies, but the nature of the compounds has not been much examined

Kruss's analyses of carefully purified and dried potassium auribromide, KAuBr_4 , were more elaborate. In some experiments the percentage of gold in the salt was determined by reduction with sulphurous acid, in others by heating the auribromide in hydrogen. With sulphurous acid the bromine in the filtrates from the precipitated gold was estimated as silver bromide, with hydrogen the loss in weight on heating in this gas, proportional to 3Br , was ascertained, and the potassium bromide dissolved from the residue by water was recovered and weighed, in addition to the gold. The results were

KAuBr_4	$\text{Au} = 100$	35 461,	whence $\text{Au} = 197\ 123^*$,
4AgBr	$= 100$	381 021,	" " $= 197\ 150^*$,
3Br	$= 100$	121 678,	" " $= 197\ 035^*$,
KBr	$= 100$	60 390,	" " $= 197\ 374^*{}^1$

The work of Thorpe and Laurie² was published in 1887. Like Kruss, they employed potassium auribromide as the basis of their research. By heating, the salt was decomposed into gold and potassium bromide, the mixture weighed and extracted with water, and the residual gold weighed. The amount of potassium bromide was ascertained by difference, and the filtrate containing this salt was analysed for bromine by titrating it against silver³ according to the procedure of Stas. The silver bromide produced was also collected and weighed. The results were

$\text{KBr} = 100$	60 331,	whence $\text{Au} = 197\ 272^*$,
$\text{Ag} \text{ Au} = 100$	182 827,	" " $= 197\ 234^*$,
$\text{AgBr} = 100$	95 208,	" " $= 197\ 248^*$

The elaborate research of Mallct³ appeared in 1889. Extreme care was exercised in this investigation, in example of the refinement of the methods employed being the substitution of quartz-sand for filter paper, to avoid reduction of the gold salts to the metal during filtration.

All Mallett's analyses of auric chloride, auric bromide, and potassium auribromide were made by the same method. The gold in one sample of the compound was determined by reducing with sulphurous acid, collecting the precipitate, heating it in the vacuum of a Sprengel pump, cooling and weighing. From another sample the halogen was precipitated by a slight excess of silver nitrate prepared from a known weight of silver and the excess of silver was determined by titration with a standard solution of hydrobromic acid. To avoid weighing the gold salts they were dissolved in water and weighed portions of the solutions were employed for the analyses. The results were

(AuCl_3)	3Ag	Au	100	60 910	whence Au	$197\ 129^*$
(AuBr_3)	3Ag	Au	100	60 927	"	$197\ 181^*$
(KAuBr_4)	1Ag	Au	100	15 659	"	$197\ 157^*$

A further series of five experiments was made to determine the ratio of the electrochemical equivalents of gold and silver, by passing the same quantity of electricity through solutions of potassium auribromide,

¹ The value calculated from the ratio $\text{Au} : \text{KBr}$ has been increased by 0.295 to correct it to vacuum standard. Compare Brünnner's *Abegg und Auersbach's Handbuch der anorganischen Chemie*, Leipzig, 1908, 2, 1, 758.

² Thorpe and Laurie, *Trans. Chem. Soc.* 1887, 51, 565-866.

³ Mallct, *Phil. Trans.* 1889, 180, 395.

derived from the nitre, which usually contains some muriates mixed with it To obtain the acid pure, the nitre should be repeatedly dissolved in warm water, and crystallized, taking out the first formed crystals for use , and the acid, when obtained, should be treated with nitrate of barytes to precipitate the sulphuric acid, and nitrate of silver to precipitate the muriatic acid

The theory of this process is well understood nitrate of potash is a compound of nitric acid and potash , sulphuric acid has a stronger affinity for potash than nitric , it therefore displaces the nitric, which with the water of the sulphuric acid and that of the nitre, is distilled by the heat, and the compound of acid and water constitutes the liquid nitric acid above Near the end of the process, the heat is advanced to 500° and upwards, and the acid is partly decomposed , some oxygen is given out, and nitrous gas, which combines with the acid, and forms *nitrous* acid vapour This acid becomes mixed with the nitric, and renders it more fuming and volatile The nitrous acid may be driven from the liquid nitric by heat, and then the last becomes less volatile, and colourless like water

The specific gravity of the liquid nitric acid ^{as obtained} is usually from 1 4 to 1 5 By

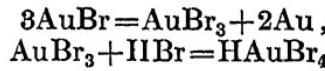
prepare it free from gold and auric chloride, and there is much divergence in the temperatures cited by various experimenters, the values ranging between 120° and 300° C¹. The auric chloride can be washed out of it by means of ether, but it is difficult to prevent decomposition of the aurous chloride into auric chloride and gold under the influence of traces of water



The decomposition by water is accelerated by rise of temperature

The chloride² is a yellowish-white substance, soluble in aqueous alkali-metal chlorides³ with formation of complex anions, the solutions soon decomposing with precipitation of metallic gold and the formation of complex auric derivatives. The transformation is more rapid in bromide solutions. At 110° to 120° C aurous chloride and excess of phosphorus trichloride combine to form a double compound of the formula $\text{AuCl}_3\text{PCl}_3$, colourless prisms insoluble in water⁴.

Aurous bromide, AuBr — When auric bromide is heated, bromine is evolved, and aurous bromide left as a green mass⁵. It is also formed by heating auribromic acid, HAuBr_4 , the auric bromide formed decomposing at 115° C. Above this temperature it is decomposed into gold and bromine, and reacts with water like aurous chloride. Aqueous hydrobromic acid converts it into gold and auribromic acid, HAuBr_4 .



It dissolves in solutions of alkali metal bromides⁶.

Aurous iodide, AuI — The iodide is produced by decomposition of auric iodide at ordinary temperature, by the interaction of auric oxide and hydriodic acid⁷, by precipitation of auric chloride with potassium iodide,⁸ hydrogen iodide, or ferrous iodide, by the interaction of gold and iodine in ether solution or in a sealed tube at 50° C, or ferric iodide, or manganese tetr碘ide⁹, by boiling powdered gold with hydriodic acid and nitric acid, filtering, and pouring the hot filtrate into aqueous hydriodic acid¹⁰ and by the interaction of aurous chloride and potassium iodide¹¹.

Aurous iodide is a lemon yellow powder, and is very difficult to prepare in the pure state as it is decomposed by moist air at ordinary temperatures. The excess of iodine is best eliminated by sublimation at 30° C. It is decomposed by heating with water dilute sulphuric acid,

¹ Dümmer *Handbuch der anorganischen Chemie* Stuttgart 1893, 3, 761. Berzelius, *Lehrbuch der Chemie* 6th ed. Dresden 1835, 1841, 4, 691. Thomsen *Thermochemische Untersuchungen* Leipzig 1882, 1883, 3, 386. Leuchs *J. prakt. Chem.* 1872 [2], 6, 156. Kruss *Innalen* 1887, 237, 276.

Compare Dümmer *J. prakt. Chem. Soc.* 1913, 35, 552.

² Langfeld *J. Amer. Chem. J.* 1901, 26, 321.

³ Lindt *Compt. rend.* 1881, 98, 1382; compare Abegg *Zeitsch. anorg. Chem.* 1904, 39, 333.

⁴ Fernand Meyer *Compt. rend.* 1909, 148, 316.

⁵ Langfeld *loc. cit.*

⁶ Compare Pelletier *Cinclin Kraut's Handbuch der anorganischen Chemie*, 6th ed., Heidelberg, 1872-1897, 3, 1015.

⁷ Fordos *J. Pharm.* 1811, 27, 653.

⁸ Compare Nielles *Ann. Chim. Phys.*, 1867 [4], 10, 318. *Compt. rend.* 1866, 62, 755, 63, 21.

⁹ Compare Cinclin Kraut *Handbuch der anorganischen Chemie* 7th ed. Heidelberg 1914, 5, II, 282.

¹⁰ Compare Fernand Meyer *Compt. rend.* 1904, 139, 733.

charcoal, essential oils, &c 7 When distilled over sulphur, it converts the sulphur into sulphuric acid 8 It oxidizes the metals, as has been observed, and gives out nitrous gas 9 When the vapour of nitric acid is passed through a red hot earthen tube, the acid is decomposed into oxygen and azote The same decomposition is effected by heating nitre red hot in an iron or earthenware retort 10 It unites to the alkalies, earths, and metallic oxides, forming salts denominated *nitrates*

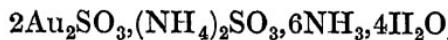
One of the most important considerations relative to nitric acid is the determination of the quantity of real acid in a watery solution of a given specific gravity This subject has engaged the attention of several eminent chemists, particularly Kirwan, Davy, and Berthollet Their results are widely different For instance, in an acid of 1 298 sp gravity, Kirwan says the real acid is $30\frac{3}{4}$ per cent Davy says 48, and Berthollet 32 or 33 (See Journal de Physique, March 1807) * My experience in regard to this particular has

* Berthollet, by mistake, makes Davy represent the acid in question to contain 54 per cent of acid, but it is the water which he says is 54 per cent and the acid 46, when the sp gravity is 1 283, so that the difference, great

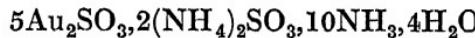
cyanide With sodium sulphide¹ and with potassium sulphide,² aurous sulphide forms double sulphides of the type NaAuS

Complex Derivatives of Aurous sulphite — Although aurous sulphite itself has not been isolated, double sulphites of aurous gold with sodium, potassium, ammonium, and barium have been obtained³. The sodium salt is formed by the interaction of auric chloride and sodium sulphite in alkaline solution, or by the action of sodium hydrogen sulphite on a boiling solution of a gold salt, or by that of sulphurous acid on a similar solution at 30° to 50° C. It has the formula $\text{Au}_2\text{SO}_3 \cdot 3\text{Na}_2\text{SO}_3 \cdot 3\text{H}_2\text{O}$ or $\text{Na}_3\text{Au}(\text{SO}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$, containing the complex anion $\text{Au}(\text{SO}_3)_2^{2-}$, since it does not display the reactions characteristic of sulphites. It is readily soluble in water.

The ammonium salt forms white needles, and the barium salt is a purple-red, amorphous substance. The constitution of the ammonium salt produced by the interaction of auric chloride and an ammoniacal solution of ammonium sulphite is uncertain, but is given as

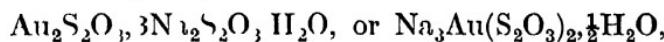


or



Aurous thiosulphate, $\text{Au}_2\text{S}_2\text{O}_3 \cdot 3\text{H}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$ — This substance is to be regarded as a complex aurothiosulphuric acid. It is prepared by the action of dilute sulphuric acid on the barium salt⁴.

Sodium thiosulphite reacts with a solution of auric chloride to form sodium aurothiosulphate,



colourless, vacular crystals. At 150° to 160° C it loses water, and at higher temperatures it is decomposed. Hydrogen sulphide and ammonium sulphide precipitate aurous sulphide from its solution and iodine transforms it into sodium tetrathionate and aurous iodide. In accordance with the presence of a complex ion hydrochloric acid and sulphuric acid do not precipitate sulphur in contrast to their action on ordinary thiosulphates. The complexity of the ion is further manifested in the inability of the usual gold reducers to precipitate the metal.

Aurous Derivatives of Nitrogen — Aurous oxide and ammonia combine to form an explosive product⁵ $\text{Au}_2\text{N} \cdot \text{NH}_3 \cdot 4\text{H}_2\text{O}$ ⁶. When boiled with water half of the nitrogen is eliminated, with formation of another nitride $\text{Au}_2\text{N} \cdot 5\text{H}_2\text{O}$. A highly explosive aurous hydrazoate has also been prepared⁷.

Aurous cyanide, AuCN — The cyanide is produced by the interaction of hydrogen cyanide and auric hydroxide⁸ by double decomposition

¹ Antony und Eucher's *Cavetta* 1896 26 II 350 Dammer *Handbuch der anorganischen Chemie*, Stuttgart 1893 3 769 Yorke *Tubag and Kopp's Jahresbericht für 1847-1848* Giesen 1849 151

² Yorke *loc. cit.* Oberl. Impf. Ann. Chem. 1811 80 140 compare Hofmann and Hochstet. Ber. 1903 36 3090

³ Haase *Einwirkung von schwefriger Säure auf Goldchlorid* Postock 1869 *Krit. Zeit. Chem.* 1869 12 535 compare Losenheim, Hertzmann and Pritze *Ztschr. anorg. Chem.* 1908 59 198

⁴ Fordos and Celsis *Ann. Chim. Phys.* 1843 [3] 13 394

Liquier *ibid.* 1844 [3] II 336

⁶ Rischig *Innalen* 1886 235 349

⁷ Curtius und Russom *J. prakt. Chem.* 1898 [2] 58 261

⁸ Dammer *Handbuch der anorganischen Chemie*, Stuttgart, 1893 3 774

Percival has noticed some results in the distillation of nitre, 2 lbs of nitre and 1 of concentrated sulphuric acid were mixed and distilled, the products were received in 3 portions, the first was of the strength 1 494, the second, 1 485, the third, 1 442 Proust, in the Journal de Physique, 1799, relates that he obtained an acid 1 52, this being again distilled, gave for the first product 1 51, for the second, 1 51, nearly colourless, which he expected indicated a superior specific gravity, but what surprised him more, was to find the residue colourless, and 1 47 This residue was distilled, the first portion was 1 49, and the rest 1 44 In another instance an acid 1 55 was obtained, this redistilled gave, first 1 62, the second 1 53, and the residue was 1 49 —From all these facts, it appeared to me reasonable to conclude that an acid of some one strength, and only one, was incapable of any change of strength by distillation, or was of such a nature, that the distilled part and the residue were always of the same strength and specific gravity The actual strength of this acid was a desirable attainment, for such an acid evidently marks a nice adjustment of affinities between the acid and water, or a kind of mutual saturation of the two By repeated experiments I find this acid to be of the specific gravity 1 42, it is

of this compound has been a matter of dispute,¹ and it has been assumed to be a molecular compound of the formula $\text{AuCl}_2\text{AuCl}_3$, containing equimolecular proportions of aurous chloride and auric chloride. Thermochemical data indicate that this assumption is incorrect.²

Gold dibromide, AuBr_2 —Bromine converts powdered gold at 170°C into the dibromide, a black substance slowly soluble in water with decomposition.³ It is also decomposed by heat, and by the action of acids. The individuality of the dibromide has also been disputed,⁴ but it is supported by thermochemical evidence.⁵

Gold monoxide, AuO —An oxide of this formula is said to be formed by the action on gold of a small proportion of *aqua regia* containing excess of hydrochloric acid, addition of sufficient primary carbonate to the solution to redissolve the precipitate first formed, and heating the solution.⁶ The product separates as an olive-green hydrate, which dries in the air to a hard mass. It is doubtful whether the oxide is a true chemical compound or not.

A hydrated gold oxide of the formula $\text{Au}_3\text{O}_2(\text{OH})_2$ is prepared by the action of boiling water on the monosulphate, AuSO_4 .⁷ It is a deep-black powder, decomposed at 160° to 205°C .

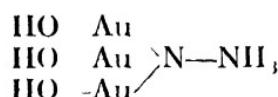
Gold monosulphide, AuS —Hydrogen sulphide or an alkali-metal sulphide precipitates the monosulphide from solutions of auric chloride,⁸ and it is also produced by the action of hydrogen sulphide on sodium aurothiosulphate. It is a black substance, insoluble in acids except *aqua regia*, but soluble in alkali-metal sulphides.⁹

Gold monosulphate, AuSO_4 —Evaporation of a solution in concentrated sulphuric acid at 250°C of the so called *acid auryl sulphate*, AuOHSO_4 (p. 347), yields large crystals of the monosulphate.¹⁰ It is characterized by its sulphurized colour. Exposure to moist air changes it into the black hydrated monoxide.

Nitride of Bivalent Gold Ammonia converts gold monoxide into a nitride containing gold and nitrogen in the atomic proportions 3 : 2, but different from the product formed by the interaction of ammonia and aurous oxide.¹¹ The reaction is possibly expressed by the equation



The substance is explosive and is regarded by Rasching as probably having the constitution



¹ Compte Kruss und Schmidt *Ber.* 1887 20 2621 *J. prakt. Chem.* 1888 [2] 38
77 Thomsen *ibid.* 1888 [2] 37 10; Petersen *ibid.* 1892 [2] 46 328

² Petersen *J. prakt. Chem.* 1892 [2] 46 328

³ Thomsen *ibid.* 1888 [2] 37 386

⁴ Kruss und Schmidt *ibid.* 1888 [2] 38 77

⁵ Petersen *ibid.* 1892 [2] 46 328

⁶ Prst. *Compt. rend.* 1870 70 840

⁷ Schottlander *Innalen* 1883 217 337

⁸ Oberlämpf *Inn. Chim.* 1811 80 110; comp. Levol *ibid.* 1850 [3] 30 356
Fellenberg *Pogg. Annalen* 1840 50 71 Hoffmann und Kruss *Ber.* 1887 20 2705

⁹ Gutbier and Durrwachter (*Zeitsch. anorg. Chem.* 1922, 121, 266) failed to prepare this substance in accordance with the literature

¹⁰ Schottlander *Innalen*, 1883 217 337

¹¹ Rasching *ibid.*, 1886, 235, 351

to calculate the real acid in the said solution. Now, 106 grains of 1 51 nitric acid + 248 grains of a solution of potash 1 482, with water, gave 665 grain measures of solution of nitre of 1 130 sp gravity, indicating 150 of pure nitre. Hence 106 grains of the acid contained 71 2, or 67 per cent which is $1\frac{1}{2}$ per cent less than Kirwan deduces it, and this may partly arise from the escape of some acid by its mixture with water producing heat. Again, 133 grains of 1 42 acid were saturated with potash, they gave 672 measures of 1 13 solution, indicating 152 nitre, hence 133 acid contained 72 real, or 54 per cent which nearly agrees with Kirwan's. Again, 205 grains of 1 35 acid were saturated with 290 grains of 1 48 carbonate of potash, this diluted gave 850 measures of 1 13 solution, indicating 192 nitre, that is, 205 grains acid contained 91 real, 44 1 per cent which also nearly agrees with Kirwan. Again, 224 grains of 1 315 acid, took 300 grains of 1 458 carbonate of potash, this diluted gave 804 measures of 1 13 solution, indicating 192 nitre, that is, 224 grains of acid contained 86 5 real, = 38 6 per cent, this is extremely near Kirwan's estimate.

Being thus satisfied with the near approximation to truth of Kirwan's table of nitric acid

A test of the purity of the salt is its complete solubility in ether.¹ It is unaffected by the prolonged action of radium bromide.²

In dissolving alloys of gold and silver in *aqua regia* in presence of ammonium chloride and nitrate, purplish-brown crystals of the formula



are sometimes obtained as a by-product.³

Aurichloric Acid, HAuCl_4 —A solution of this substance is produced by the action of hydrochloric acid on auric chloride, or by addition of excess of this acid to a solution of gold in *aqua regia* to decompose the nitric acid present. It crystallizes in yellow needles, which deliquesce in moist air to a yellow solution.⁴ The acid exists in the form of two distinct hydrates, one with three⁵ and the other with four⁶ molecules of water, the individuality of the two being indicated by the heats of solution.⁷ In the solution of this acid the gold is present in the anion AuCl_4^- .⁸ Its action on potassium ferrocyanide has been investigated.⁹

A great number of *aurichlorides* is known. **Potassium aurichloride, KAuCl_4** , is prepared in the anhydrous form by evaporating a solution of auric chloride in concentrated hydrochloric acid in presence of potassium chloride.¹⁰ It melts at the temperature of boiling mercury.¹¹ It is also known as *semihydrate* and *dihydrate*.¹² It dissolves readily in water. Heating converts it into potassium aurochloride, KAuCl_2 .

Sodium aurichloride, $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$, forms rhombic columnar crystals or laminae.¹³ Its water of crystallization cannot be expelled without decomposing the salt, a distinction from the potassium derivative. Its solubility in ether is another characteristic point of difference.¹⁴ It can be employed as a test for iodides in presence of bromides, the liberated iodine imparting a violet colour to chloroform.¹⁵

Two ammonium aurichlorides are known:



The first is prepared in yellow, monoclinic plates from a solution of auric chloride in concentrated hydrochloric acid in presence of ammonium chloride, the second in yellow laminae from a neutral or slightly acidic solution of auric chloride. At 100° C they give up their water of crystallization and at higher temperatures decompose.

¹ Ern. Schaeff. *Wochenschr. Chem. Pharm.* 1913, 51, 386
Ern. *Trans. Chem. Soc.* 1908, 93, 1775

² Pollard *ibid.* 1920, 117, 99

³ Leizelius *Lehrbuch der Chemie*, 5th ed., Dresden, 1813-1818, 4, 692

Weber *Logg. Annal. n.* 1867, 131, 41; Schottlander *Annalen* 1883, 217, 312

⁴ Thomsen *Thermodynamische Untersuchungen*, Leipzig, 1882-1883, 3, 382

⁵ Compare Lenzfeld *Angew. Chem. J.* 1901, 26, 321; Schmidt *Apotheker Zeit.* 1906, 21, 661

⁶ Hittorf *Logg. Annal. n.* 1859, 106, 523

⁷ Peutel *Monatsh.* 1910, 31, 571

⁸ Lunge *ibid.* 1890, 11, 220

⁹ Ephrussi *La.* 1919, 52 [B], 211

¹⁰ Topsöe *Gmelin-Kraut's Handbuch der anorganischen Chemie*, 6th ed., Heidelberg, 1872-1897, 3, 1030

¹¹ Compare Topsöe *Ib. cit.*

¹² Finschender *Nedel. Tijdsch. Pharm.* 1891, 6, 1, 227

¹³ Leichhardt *Pharm. Zeit.* 1909, 54, 58

¹⁴ Topsöe *Gmelin-Kraut's Handbuch der anorganischen Chemie*, 6th ed., Heidelberg, 1872-1897, 3, 1026

¹⁵ Topsöe *ibid.* (with Darmstädter and Förchheimer)

potash, gave 66 grains of nitre, at 212° , and this became 60 by fusion in the other, 90 grains of 1 504 acid, saturated with potash, gave 173 of dry nitre — In all the similar experiments which I have made, I have uniformly found only *three quarters* of the quantity of nitre said to have been obtained above, from given quantities of the acid I conclude, therefore, that Mr Davy must have committed some oversight in these two experiments, and that the direct formation of nitre from nitric acid and potash, accords only with Kirwan's estimate of the strength of nitric acid

Berthollet, in the Journal de Physique, March 1807, informs us, that he saturated 100 parts of potash with nitric acid of 1 2978 strength, and obtained 170 parts of nitre, he calculates the acid to contain 32 41 per cent real, by which we may infer that 216 grains of it were required Nitre, according to this, would be 100 potash + 70 nitric acid, or 59 potash + 41 acid per cent This is much more potash than ever before was detected in nitre How are we to be satisfied that the potash used contained no water? If it contained any water, this would disappear in the process, and its weight be supplied by nitric acid, which would not be placed to the acid's account That this was the real fact I have no

powder At 160° C it is completely transformed into aurous bromide¹ in the form of a green mass,² and bromine When prepared by the action of bromine on precipitated gold, it forms black crystals, volatile in bromine at 300° C ²

Auribromic Acid, HAuBr_4 —Solutions of auric bromide and of gold in bromine-generating liquids are converted by hydrogen bromide into a solution of auribromic acid The substance is also formed in solution by the action of the same reagent on a solution of auric chloride, and can be extracted by ether from the dark-red liquid³ Evaporation of the concentrated aqueous solution yields the acid in dark-red crystals of the formula $\text{HAuBr}_4 \cdot 5\text{H}_2\text{O}$ ⁴ or $\text{HAuBr}_4 \cdot 6\text{H}_2\text{O}$,⁵ melting at 27° C in its own water of crystallization, and decomposed by concentrated sulphuric acid at 155° C into aurous bromide and bromine⁶

Potassium auribromide, KAuBr_4 , is produced by the action of bromine on gold and the equivalent proportion of potassium bromide⁷ On evaporation of the solution, potassium auribromide crystallizes in dark-red prisms containing two molecules of water of crystallization⁸, and by drying the crystals over phosphoric oxide it is obtained in the form of purple-red, monoclinic crystals⁹ free from water On exposure to air, it takes up two molecules of water¹⁰ Its solubility at 15° C is 19.53 grams in 100 grams of water

Ammonium auribromide, NH_4AuBr_4 , is produced by the action of ammonia on the acid, and forms bluish-black crystals of fat-like lustre The anhydrous rubidium and caesium salts give prisms of metallic lustre, the colour of the first being cinnabar-red, and of the second deep black¹¹

Auribromides of sodium, barium, zinc, manganese,¹² and magnesium¹³ have been prepared Triple bromides of gold, silver, and rubidium (or cesium) have also been described¹⁴ Double compounds of auric bromide and phosphorus derivatives can be obtained by methods similar to those employed for the corresponding chlorine addition-products¹⁵

Auric iodide, AuI_3 Gradual addition of a solution of auric chloride to one of potassium iodide yields complex AuI_4^- ions, converted by further addition of auric chloride into auric iodide¹⁶



On drying the dark green product decomposes into aurous iodide and iodine It is soluble with difficulty in water to an unstable solution

¹ Schmidt *Chem Zeit* 1896 20 483

Ferdinand Meyer *Compt rend* 1909 148 316

² Cuthbert and Huber *Zeits anorg Chem* 1914 85 353 compare *Gmelin Kraut's Handbuch der anorganischen Chemie* 6th ed Heidelberg 1872-1897 3 1016

³ Thomsen *Thermochimische Untersuchungen* Leipzig 1882-1883 3, 390

⁴ Langfeld *Angew Chem* 1901 26 321

⁵ Schmidt *Chem Zeit* 1896 20 483

Schottlander *Annal n* 1883 217 315

⁶ Cuthbert and Huber *loc cit*

⁷ Compare Muthmann *Annalen* 1887 237 259 Bonsdorff *Jogg Annalen* 1830

⁸ 19 346 1831 33 64

⁹ Compare Muthmann *loc cit*

¹⁰ Cuthbert and Huber *loc cit*

¹¹ Bonsdorff *Jogg Annalen* 1829 17 261 1831 33 64

¹² Fuchs *J prakt Chem* 1872 [2] 6 156

¹³ Bunsching *Monatsh* 1921 42 399

¹⁴ Lindert *Compt rend* 1885 101 164

¹⁵ Johnston, *Phil Mag* 1836, 9 266

except the first and second column, which his table has not, and the three last, where I think he has overrated the quantity of acid, indeed, the lower part of his table is confessedly less correct I have already given my reasons for considering his table as approximating nearest to the truth, but have no doubt it might be made more correct, I have, therefore, only extended the table to two places of decimals in the column of specific gravity The column of acid per cent by measure, will be found convenient for the practical chemist The first column shews the number of atoms of acid and water in combination or collocation in each solution, agreeably to the preceding determinations, namely, an atom of acid is taken as 19 1 by weight, and an atom of water as 8 The last column exhibits the boiling points of the several solutions, as found by experiment Those who wish to repeat these experiments, may be informed that a small globular glass receiver, of the capacity of 6 or 7 cubic inches was used, 2 or 3 cubic inches of acid were put in, and then a loose stopper It was then suspended over a charcoal fire When signs of ebullition began to appear the stopper was withdrawn, and a thermometer, previously adjusted at the boiling point of wa-

produced, and addition of sulphuric acid liberates auric hydroxide, $\text{AuO(OH)} \cdot \text{H}_2\text{O}$, which is converted by alkalies into the corresponding aurate, $\text{M}'\text{AuO}_2$ or $\text{M}''(\text{AuO}_2)_2$, containing water of crystallization. The products are pale-green, acicular crystals, the dry salts being stable to heat. They are reduced by sulphurous acid and by alcohol to metallic gold. Dilute sulphuric acid and nitric acid yield the corresponding metallic nitrate and auric hydroxide, hydrochloric acid produces the metallic chloride and auric chloride. The calcium, barium, and magnesium salts are not readily soluble in water.¹

A complex derivative of auric oxide and higher oxides of manganese has been described.²

Auric sulphide, Au_2S_3 —Gold does not combine directly with sulphur,³ but at -2°C a rapid current of hydrogen sulphide transforms aurichloric acid, HAuCl_4 , in dilute solution in normal hydrochloric acid, into pure auric sulphide.⁴ Lithium aurichloride, $\text{LiAuCl}_4 \cdot 2\text{H}_2\text{O}$, at -10°C is converted by hydrogen sulphide into a mixture of lithium chloride and impure auric sulphide, with evolution of hydrogen chloride. After extraction of the lithium chloride with alcohol, the sulphide is dried in a current of nitrogen at 70°C .⁵ It is an amorphous, black powder, at once decomposed by the action of water. At 200° to 205°C it is converted into a mixture of gold and sulphur. It forms double sulphides with the alkali metals⁶, and also unites with the sulphides of elements of weak positive, or even of negative, character, such as arsenic, tellurium, molybdenum, and carbon.⁷ The last class of compound is probably to be regarded as an auric salt of a complex acid containing sulphur and one of the elements mentioned.

Auric sulphate, $\text{Au}_2(\text{SO}_4)_3$ —The sulphate has not been isolated. Gold dissolves in concentrated sulphuric acid in presence of a small proportion of nitric acid, forming a yellow liquid, but dilution precipitates the gold either as the hydroxide, or in presence of reducers as the metal.⁸ The nitric acid can be replaced by other oxidizers, such as iodic acid⁹ and manganese dioxide¹⁰, and a solution of the sulphate is also formed by the action of concentrated sulphuric acid on auric oxide.¹¹

Acid auryl sulphate, AuOHSO_4 —This sulphate is produced by the action of concentrated sulphuric acid on auric hydroxide at 180°C , the brown basic salt formed being converted by heating at 200°C into the yellow acid auryl sulphate.¹² It is decomposed by water with formation of auric hydroxide, but dissolves in concentrated sulphuric acid to a yellowish red solution from which it separates unchanged. When this acid solution is heated with potassium hydrogen sulphate, a yellow, crystalline salt of the formula $\text{KAu}(\text{SO}_4)_2$ separates. It is more stable than acid auryl sulphate, but is slowly decomposed by water, with

¹ Weiz und Zeitsch angew Chem 1906 19 139

Schottlander Annalen 1883 217 310

² Petibon Compt rend 1909 148 1176 Ann Chim Phys 1909 [8] 17 526

³ Cuthbert und Durrwachter Zeitsch angew Chem 1922 121 266

Antony und Lucchesi Gazzetta 1889 19 515 1890 20 601

⁴ Ditte Ann Chem Phys 1907 [8] 12 229

⁵ Perzelius Lehrbuch der Chemie 5th ed Dresden 1813-1818 3 698

⁶ Reynolds Chem News 1861 10 167 Spiller ibid 173 Allen ibid 1872 25 85

⁷ Pict. Dinglers Polytech J 1870 198 59

⁸ Lenher Electrochem Ind 1901 2 316

⁹ Compare Gmelin Krut, Handbuch der anorganischen Chemie, 6th ed Heidelberg, 1872-1897, 3 1014

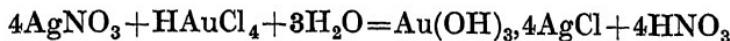
¹⁰ Schottlander Wied Annalen 1883 217 368

Remarks on the above Table

I It seems not improbable, but that an acid free from water may be obtained, as represented in the first line of the table That such an acid would be in the liquid state, but with a strong elastic steam or vapour over it, at the common temperature, is most probable , in this respect it would resemble ether, but perhaps be more volatile Seventeen per cent of water would bring it down to acid of the second line, and such as has actually been obtained by Proust This last would nearly agree with ether in volatility With respect to the specific gravity of pure nitric acid, it must be less than 1 8 , because a measure of that sp gravity mixed with a measure of water, would make 2 measures of 1 4, if there were no increase of density , and acid of this density is nearly half water * I apprehend if

* The theorem for specific gravities is $\frac{H}{S} + \frac{L}{s} = \frac{H+L}{s}$, where H represents the weight of the body of greatest specific gravity, S its specific gravity, L the body of least specific gravity, s its specific gravity, and s that of the mixture or compound Hence in the case above, $\frac{18}{18} + \frac{1}{1} = \frac{28}{14}$

Silver nitrate reacts with aurichloric acid in accordance with the equation



The brown precipitate formed is converted by ammonia into fulminating gold, which after drying explodes violently downwards when touched with a knife. Jacobsen regards it as having the constitution $\text{Au(OH)}_2 \text{NH}_2$ or $(\text{AuN}, 2\text{H}_2\text{O}) \cdot \text{H}_2\text{O}$. When boiled with potassium-hydroxide solution, it is converted into a blackish brown substance of even more explosive character, probably having the constitution $\text{Au(OH)}_2 \text{NH Au(OH)}_2$.

Auric nitrates — Complex derivatives with the anion $\text{Au(NO}_3)_4'$ are known. Auric hydroxide and nitric acid yield a substance of the formula $\text{HAu(NO}_3)_4 \cdot 8\text{H}_2\text{O}$, crystallizing in octahedra, and soluble in concentrated nitric acid.¹ Aurinitric acid melts at 72° to 73°C , and its density is 2.84. When heated above its melting point, it is converted into a black substance, possibly auric nitrate, $\text{Au(NO}_3)_4$. Aurinitrates of rubidium, potassium, thallium, and ammonium have been prepared. From the ammonium salts a yellowish brown, explosive substance, similar in properties to fulminating gold, has been obtained. Several basic nitrates of gold are also known.

Compounds of Gold and Phosphorus — Phosphine reacts with a solution of auric chloride in anhydrous ether, forming *auric phosphide*, AuP , a substance decomposed by water or potassium-hydroxide solution, with formation of phosphine and phosphoric acid.² At 100° to 110°C it undergoes oxidation in the air. Heating in a current of carbon dioxide causes volatilization of phosphorus. Nitric acid oxidizes the phosphorus, leaving a residue of metallic gold. These reactions indicate the substance to be an alloy of gold and phosphorus.

Gold phosphides — *Gold sesquiphosphide*, Au_2P_3 , is said to be formed by heating phosphorus with gold.³

Another phosphide, Au_3P_4 , is produced by the interaction of phosphorus vapour and gold.³ It is a grey brittle substance of density 6.67 and is formed only in the neighbourhood of 400°C .⁴ Acids react with it as with an alloy.

Gold arsenides — Arsenic precipitates from auric chloride solution in arsenide Au_2As .⁵ Fusion of this substance with potassium cyanide converts it into a yellow arsenide, Au_4As_3 , of density 16.2. Both substances have the character of alloys.

Auric antimonide, AuSb . This substance is a white brittle product, of density 11.13.⁶ It behaves as an alloy. Other alloys of gold and antimony are known.⁷

Auric cyanide, Au(CN)_4 . Potassium auricyanide is transformed by strong acids such as hydrofluosilicic acid into auric cyanide. The reaction is more complex than is indicated by the equation:



¹ Schottländer *Wied. Annalen* 1883, 217, 356
Cavazzi *Cavazza* 1885, 15, 40

² Schrotter *Sitzungsber. K. Akad. Wiss. Wien* 1849, 2, 308

³ Granger *Compt. rend.* 1897, 124, 498

⁴ Desormes *ibid.* 1878, 86, 1022 Lindbom *Bull. Soc. chim.* 1878 [2], 29, 416

⁵ Christoffle *Combinaisons de l'Antimoine* Göttingen 1863

⁶ Compere Dimmert *Handbuch der anorganischen Chemie* Stuttgart 1893, 3, 773

Remarks on the above Table

I It seems not improbable, but that an acid free from water may be obtained, as represented in the first line of the table That such an acid would be in the liquid state, but with a strong elastic steam or vapour over it, at the common temperature, is most probable , in this respect it would resemble ether, but perhaps be more volatile Seventeen per cent of water would bring it down to acid of the second line, and such as has actually been obtained by Proust This last would nearly agree with ether in volatility With respect to the specific gravity of pure nitric acid, it must be less than 1 8 , because a measure of that sp gravity mixed with a measure of water, would make 2 measures of 1 4, if there were no increase of density , and acid of this density is nearly half water * I apprehend if

* The theorem for specific gravities is $\frac{H}{S} + \frac{L}{s} = \frac{H+L}{J}$, where H represents the weight of the body of greatest specific gravity, S its specific gravity, L the body of least specific gravity, s its specific gravity, and J that of the mixture or compound Hence in the case above, $\frac{18}{18} + \frac{1}{1} = \frac{28}{14}$

chlorides by heating the sulphides with a mixture of potassium nitrate and ammonium chloride¹

The metal can also be precipitated with hydrazine chloride in alkaline solution². The precipitate is freed from mercury, copper, cadmium, and bismuth by extraction with nitric acid, and the residual gold and platinum dissolved in *aqua regia*. The gold is precipitated from this solution by the action of sodium hydroxide and hydroxylamine, the platinum remaining dissolved. Another method is to precipitate tin, lead, and bismuth with ammoniacal hydrogen peroxide, eliminate the hydrogen peroxide, and precipitate the gold with the mercury and part of the platinum by heating with hydroxylamine.

The presence of gold in any of the precipitates described can be detected by solution in *aqua regia*, and reduction to metallic gold by various reagents, including ferrous chloride, ferrous sulphate, mercurous nitrate, stannous chloride, hypophosphorous acid, oxalic acid,³ sulphurous acid, hydrogen peroxide and potassium hydroxide, formaldehyde, and hydroxylamine hydrochloride⁴.

Among the reagents applicable to the detection of small quantities of gold⁵ are alkaline hydrogen peroxide, ferrous salts, stannous chloride, which gives the characteristic purple coloration with one part in 100,000,000 parts of solution, alkaline formaldehyde, which gives a violet coloration with one part in 100,000 parts of solution⁶, and titanium trichloride, $TiCl_3$, which gives a deep-violet coloration with one part in 20,000,000 parts of solution, the action resembling that of stannous chloride⁷.

A colorimetric test described by Pollard⁸ depends on the production of a bright yellow coloration when a 0.1 per cent solution of o toluidine in hydrochloric acid of 10 per cent strength is added to a solution of auric chloride containing one part of gold in 1,000,000 parts of water. Osmic acid, mordates, and salts of ruthenium and of iron also give a yellow coloration and in presence of copper a green coloration may be obtained instead of a pure yellow colour. Other metals do not interfere with the test but traces of hypochlorites give a grass green coloration.

A method of detection by means of the metaphosphate bond has also been described⁹.

One tenth of a microgram of gold can be detected by Bayer's microchemical method mentioned in connexion with rubidium (p. 199) and caesium (p. 210).

Gold is estimated quantitatively by methods similar to those employed in its qualitative detection. It can be precipitated with a standard solution of ferrous sulphate or potassium oxalate¹⁰ and the excess estimated by titration with permanganate, or precipitated with stannous chloride in alkaline solution the excess of tin being ascertained by titration with iodine¹¹. Other methods are direct titration with stannous

¹ Fresenius *Zeitsch anal Chem* 1886 25 200

Knoevenagel and Ebeler *Ber* 1902 35 3055

² Compare Purgotti *Zeitsch anal Chem* 1870 9 127

³ Lamer *Dinglers Polytech J* 1892 284 17

Compare Lassen *Methoden der analytischen Chemie* Brunswick 1901 1 239

⁴ Armati and Barbini *Zeitsch Chem Ind Kolloide* 1910 6 290

⁵ Stähler and Bachran *Ber* 1911 44 2906

⁶ Pollard *Analyst* 1919 44 94

⁷ Donau *Zeitsch Chem Ind Kolloide* 1908 2 9 273

⁸ Franceschi *Apothek Zeit* 1894 9 121

⁹ Franceschi *Zeitsch anorg Chem* 1892 1 238

be obtained by repeated distillations of any acid above 1 42, provided there is a sufficient quantity of that, and the first products always taken. What the distinguishing properties of this acid may be, I have not had an opportunity of investigating.

4 The acid which consists of 1 atom of acid and 2 of water, is possessed of striking peculiarities. It is in fact that which constitutes a complete reciprocal saturation of the two elements. Evaporation produces no change in its constitution, it distills as water, or any other simple liquid does, without any alteration. It acquires the temperature 248° at boiling, which is greater than any other compound of the two elements acquires. At any strength above this, the acid is most copiously elevated by heat, at any strength below, the water is most easily raised. Pure water boils at 212°, pure acid perhaps at 30°, the union of both produces a heavier atom than either, and requires a higher temperature for ebullition, but in proportion as either principle prevails more than is necessary for saturation, then the temperature at ebullition is reduced towards that of the pure element itself. Proust has observed that nitric acid of 1 48, produces no more effervescence with tin than with sand, whereas the lower acids act

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5 The acid composed of 1 to 3 water, has not any peculiarity yet discovered.

6 The acid of 1 to 4 water, is remarkable for being that which freezes the most easily of all, namely at -2° of Fahrenheit, according to Cavendish. The strength of the acid is such, as that 1000 parts dissolve 418 of marble. Now, 418 of marble contain 228 of lime, and these require 370 or 380 of nitric acid, which therefore agrees with the acid of 1 to 4 water, and with that only. Above that strength, or below, the acid requires a greater cold to freeze it—The inferior acids appear to have no remarkable differences, except such as the table shews, but the temperature of freezing descends to some undetermined point, and then ascends again.

7 The notion of those who consider the intensity of acid solutions to be proportionate to the quantity per cent of the acid, or to their density, seems incorrect as far as nitric acid is to determine. It is true, the acidity or sourness of the solution, the power to produce effervescence with carbonates, and perhaps other properties, increase nearly as the quantity or strength, but the freezing and boiling temperatures, the action on metals, as tin, &c have successive waves, and abrupt termi-

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tering with the air, (except the steam which gases commonly have, the quantity of which is easily ascertained for any temperature) The instant the two gases were mixed, the globe was filled with dense orange coloured gas, which continued without any change, a dewy appearance on the inside of the glass was always perceived, consisting, no doubt, of condensed acid and water

The results of the experiments are below

	oxygen	nitrous gas	per cent
1 — 1 measure took 1 8, residuary	13 6 oxyg		
2 — 1 — — — 2 11 — — —	6	nitrous	
3 — 1 — — — 1 44 — — —	27	oxyg	
4 — 1 — — — 1 83 — — —	4	—	
5 — 1 — — — 2 29 — — —	2 5	nitrous	
6 — 1 — — — 1 61 — — —	7 6	oxyg	
7 — 1 — — — 1 65 — — —	9 3	nitrous	
8 — 1 — — — 1 8 — — —	2 5	oxyg	

The residuary gas was examined after letting in water, and washing away the acid From these results, it is evident the quantity of nitrous gas combining with a given volume of oxygen in such circumstances, is extremely variable, and much like what takes place in small quantities in tubes The coloured gas

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 Cray I A 269
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different qualities at different periods of the decomposition By one experiment, I obtained about 30 grains of air from 100 of nitre in an iron retort , it was received in 5 portions the first contained 70 per cent of oxygen, agreeing with the constitution of nitric acid exhibited in the table, page 331 , but the succeeding portions gradually fell off, and the last contained only 50 per cent oxygen

It may be proper to remark, that the nitric acid of commerce is sold under the names of double and single *aqua fortis* , the former is intended to be twice the strength of the latter, the absolute strength of double aqua fortis is not, I believe, uniform It commonly runs between the specific gravities of 1 3 and 1 4

4 Oxynitric Acid

The existence of oxynitric acid is inferred from the combination of oxygen and nitrous gas, in the second experiment, page 328 , at least an acid product is obtained, containing more oxygen than is found in nitric acid As yet I have not been able to obtain this acid any other way, and therefore have not had an

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5 N₂O Acid

The compound denominated nitrous acid, is obtained by impregnating liquid nitric acid with nitrous gas. This acid, however, is never pure nitrous acid, but a mixture of nitric and nitrous, as is evident by boiling it, when the nitrous is driven off, and the nitric remains behind. Pure nitrous acid seems to be obtained by impregnating water with oxygenous gas, and then with nitrous gas, in this way 1 measure of oxygen takes about $3\frac{1}{2}$ of nitrous, that is, 1 atom of oxygen takes 2 atoms of nitrous gas to form 1 of nitrous acid. The weight of the atom therefore is 31 2.

By repeated trials I find that 100 measures of nitric acid of 1 30 specific gravity, agitated with nitrous gas, takes up about 20 times its bulk of the gas. If the acid be of twice the strength, or of half the strength, it makes little difference, the quantity of gas is nearly as the real acid, within certain limits of specific gravity. Very dilute acid (as 1 to 300 water) seems to have scarcely any power of absorbing nitrous gas, besides what the water itself has. Hence, it seems that what we call nitrous acid,

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combines with the alkalies so as to form dry salts or *nitrates*, the concentrated solutions seem to lose the nitrous gas, and then the *nitrates* are obtained

SECTION 3

OXYGEN WITH CARBONE.

There are two compounds of oxygen and carbone, both elastic fluids, the one goes by the name of *carbonic acid*, the other *carbonic oxide*, and it appears by the most accurate analyses, that the oxygen in the former is just double what it is in the latter for a given weight of carbone. Hence, we infer that one is a binary, and the other a ternary compound, but it must be enquired which of the two is the binary, before we can proceed according to system. The weight of an atom of carbone or charcoal, has not yet been investigated. Of the two compounds, carbonic acid is that which has been longest known, and the proportion of its elements more generally investigated. It consists of nearly 28 parts of charcoal by weight, united to 72 of oxygen. Now

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electric shocks into oxygen and carbonic oxide, but carbonic oxide does not appear to be resolved in the same mode into charcoal and carbonic acid, which one might expect from a triple compound. One of the most common ways of obtaining carbonic oxide, is to decompose carbonic acid by some substance possessing affinity for oxygen, now, oxygen may be abstracted from a body possessing two atoms of it more easily than from one possessing only one. On all these accounts, there can scarcely be a doubt that carbonic oxide is a binary, and carbonic acid a ternary compound.

1 Carbonic Oxide

This gas was discovered by Dr Priestley, but its distinguishing features were more fully pointed out by Mr Cruickshanks, in an essay in Nicholson's Journal, 1801. About the same time, another essay of Desormes and Clement was published in the Annales de Chemie, on the same subject. These essays are both of great merit, and highly creditable to their authors. Before that time, carbonic oxide had been confounded with the combustible gases composed of carbone and hydrogen,

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of this process is manifest, chalk consists of carbonic acid and lime, the carbonic acid is disengaged by heat, and is immediately exposed to the red hot iron, which in that state has a strong affinity for oxygen, the carbonic acid parts with one half of its oxygen to the iron, and the residue is carbonic oxide, but part of the acid escapes along with it undecomposed. With a proper apparatus, the gas may be procured by transmitting carbonic acid repeatedly over red hot charcoal in an iron or porcelain tube.

This gas may be obtained, by exposing to a red heat, a mixture of charcoal with the oxides of several metals, or with carbonate of lime, barytes, &c. But there is great danger in this way of procuring some hydrogen, and carburetted hydrogen, along with carbonic oxide and acid. Indeed, all gas procured from wood and from moist charcoal, is a mixture of these four, varying in proportion according to the heat and the continuance of the process.

According to Cruickshanks, the specific gravity of carbonic oxide is .956, according to Desormes and Clement, .924. Apprehending that they had both rated it too low, I carefully found the specific gravity of a mixture of 6 parts carbonic oxide and 1 common air at two trials in one it came out .945,

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100 measures of carbonic oxide are mixed with 250 of common air, (in which case the whole of the combustible gas should combine with the whole of the oxygen) a smart explosion ensues by the first spark , but only $\frac{2}{3}$ ds of the gas is burnt , the rest, and a corresponding proportion of oxygen, remain in the residuum. When plenty of combustible gas and a minimum of oxygen are exploded, the whole of the oxygen usually disappears

Carbonic oxide does not explode by electricity when mixed with oxymuriatic acid, at least in any instance I have had, unless a small portion of common air be present , but the mixture being exposed to the sun, a diminution soon takes place , if the light be powerful, 5 or 10 minutes are sufficient to convert 100 grain measures of the gas along with 100 of the acid, into carbonic and muriatic acids I have n't been able to determine, from the lateness of the season (October), whether the mixture would explode by the solar light

Pure carbonic oxide is not at all affected by electricity I was present when Dr Henry conducted an experiment, in which 35 measures of carbonic oxide received 1100 small shocks , no change of dimensions took place , there was no carbonic acid formed, nor oxy-

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Cruickshanks certainly underrates the oxygen , I always find the oxygen fully equal to half the carbonic acid, whether fired over mercury or water Desormes' experiments were made over water, and are therefore rather uncertain as to the quantity of acid , they have evidently used impure gas Their first result given above is the mean of nine experiments , the other two are extremes in regard to acid and oxygen (Annales de Chimie 39— page 38) It is remarkable, that in one of their deductions (page 44), on which they seem to rely most, they find the carbone 44, and the oxygen 56 parts by a previous experiment, they had found carbonic acid to consist of 28 1 carbone, and 71.9 oxygen (page 41), that is, of 41 carbone, and 112 oxygen where the oxygen is just double of that in the carbonic oxide to a given quantity of carbone This most striking circumstance seems to have wholly escaped their notice

The exact composition of this gas is easily ascertained by exploding it with common air over water Let 2 parts of the gas be mixed with 5 of air, and fired , the residuum must be washed in lime water, and the quantity left accurately noted , then apply a small portion of nitrous gas to the residuum, sufficient to take out the oxygen hence we have data to find

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2. *Carbonic Acid*

The gas now denominated carbonic acid, has been recognised as an elastic fluid distinct from atmospherical air, for a longer time perhaps than any other. It may be said to have

gases that have been considered as belonging to these two species, are in fact oxy carburetted hydrogen, and that these elements are combined in an indefinite variety of proportions. That the combustible gases produced from moist charcoal and other bodies, contain oxygen, carbone, and hydrogen in various proportions, is a fact of which no experienced person can doubt, but it has not yet been shewn satisfactorily by any one, that they cannot be made by mixing certain proportions of two or more of the following distinct species, namely, carburetted hydrogen (of stagnant water), carbonic oxide, olefiant gas, and hydrogen.—As for carbonic oxide, whilst it remains an undisputed fact, that *in the combustion of it nothing but carbonic acid is produced, and that equal in weight to the carbonic oxide and the oxygen, it will require very specious reasoning to convince any one that it contains either hydrogen, sulphur, or phosphorus*, unless it be first proved that carbonic acid contains the same. One argument of Berthollet is, however, more ingenious than any reply to it which has appeared—it is this, *a compound elastic fluid ought to be found specifically heavier than the lighter of the two elementary fluids constituting it*. This is, as far as I know, universally true, but it does not follow that carbonic oxide should be specifically heavier than oxygenous gas. An atom of char-

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Carbonic acid gas is formed by burning charcoal, but it is most easily obtained in a pure state from chalk, or some of the carbonates, by means of dilute sulphuric or other acid, it may be received in bottles over mercury or water, but the latter absorbs a portion — This gas extinguishes flame, and is unfit for respiration, its specific gravity is nearly 1 57, as appears from the experience of all who have tried 100 cubic inches, at the pressure of 30 inches of mercury, and temperature of 60°, weigh from 47 to 48 grains Carbonic acid is frequently produced in mines, and in deep wells it is known to workmen by the name of *choak damp*, and proves fatal to many of them, it is also constantly found in the atmosphere, constituting about $\frac{1}{100}$ th part of the whole, its presence is easily detected by lime water, over which it forms a film almost instantly In the breathing of animals this gas is constantly produced, about 4 per cent of the air expired by man, is usually carbonic acid, and the atmospheric air inspired loses the same quantity of oxygen

Water absorbs just its own bulk of carbonic acid gas, that is, the density of the gas in the water after agitation, is the same as the density of the incumbent gas above, and the elasticity of the gas in the water is unimpaired The

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phosphate of lime and charcoal were obtained

Carbonic acid is decomposed by electricity into carbonic oxide and oxygen I assisted Dr Henry in an experiment by which 52 measures of carbonic acid were made 59 measures by 750 shocks , the gas after being washed became 25 measures , whence these had arisen from the decomposition of 18 measures of acid , these 25 measures consisted of 16 carbonic oxide and 9 oxygen , for, a portion being subjected to nitrous gas, manifested $\frac{1}{3}$ of its bulk to be oxygen , and the rest was fired by an electric spark, and appeared to be almost wholly converted into carbonic acid

Carbonic acid then appears to be a ternary compound, consisting of one atom of charcoal and two of oxygen , and as their relative weights in the compound are as 28 72, we have 36 28 7 5 4 = the weight of an atom of charcoal , and the weight of an atom of carbonic acid is 19 4 times that of hydrogen The diameter of an atom of the acid in an elastic state is almost exactly the same as that of hydrogen, and is therefore represented by 1 , consequently a given volume of this gas contains the same number of atoms as the same volume of hydrogen

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rate of sulphur, as its formation is similar to that of muriate of iron, &c in like circumstances Now, it has been shewn that oxy-muriatic acid is muriatic acid united to oxygen, one atom to one, hence the atom of oxygen oxidizes an atom of sulphur, and the muriatic acid unites to the oxide, forming muriate of sulphur, or more strictly *muriate of oxide of sulphur* This oxide of sulphur, Dr Thomson finds, is not easily obtained separate, for when the red liquid is poured into water, the oxide resolves itself into sulphur and sulphuric acid (Nicholson's Journal, vol 6—104)

When sulphuretted hydrogen gas and sulphurous acid gas are mixed over mercury, in the proportion of 6 measures of the former to 5 of the latter, both gases lose their elasticity, and a solid deposit is made on the sides of the tube The common explanation given of this fact is, that the hydrogen of the one gas unites to the oxygen of the other to form water, and the sulphur of both gases is precipitated This explanation is not correct, water is indeed formed, as is stated, but the deposition consists of a mixture of two solid bodies, the one sulphur, the other sulphurous oxide they may be distinguished by their colour, the former is yellow, the latter bluish white, and when they are both thrown into water, the former

soon falls down, but the latter remains for a long time suspended in the water, and gives it a milky appearance, which it retains after filtration. It will appear in the sequel, that 5 measures of sulphurous acid contain twice as much oxygen as the hydrogen in 6 measures of sulphuretted hydrogen require, it follows, therefore, that one half of the oxygen ought still to be found in the precipitate, which accords with the above observation. Again, if water, impregnated with each of the gases, be mixed together till a mutual saturation takes place, or till the smell of neither gas is observed after agitation, a milky liquid is obtained, which may be kept for some weeks without any sensible change or tendency to precipitation. Its taste is bitter and somewhat acid, very different from a mere mixture of sulphur and water. When boiled, sulphur is precipitated, and sulphuric acid is found in the clear liquid. The milkiness of this liquid seems therefore owing to the oxide of sulphur.

It may be proper to remark that the white flowers of sulphur, commonly sold by the druggists, are not the oxide of sulphur. They are obtained by precipitating a solution of sulphuret of lime by sulphuric acid. They consist of 50 per cent sulphate of lime and 50 of sul-

phur, in some state of combination with the sulphate, for, the two bodies are not separable by lixiviation

When sulphur in a watch glass is ignited, then suddenly extinguished, and placed on a stand over water, and covered with a receiver, the sulphur sublimes and fills the receiver with white fumes On standing for some minutes or an hour, the sulphur gradually subsides, and forms a fine yellow film over the surface of the water The air in the receiver loses no oxygen by this process But when sulphur ignited, is placed in the circumstances above-mentioned, it burns with a fine blue flame, emitting some bluish white fumes, scarcely perceptible at first, as the combustion continues these fumes increase, and towards the conclusion, when the oxygen begins to be deficient, they rise up in a copious stream, and fill the receiver so that the stand is scarcely visible If a portion of the air is passed through water, it still continues white In the space of an hour the air in the receiver becomes clear, but no traces of sulphur are seen on the surface of the water The whiteness in this last case does not, therefore, seem to arise from sublimed sulphur, but from the oxide of sulphur, which is formed when there is not oxygen sufficient to form sulphurous acid, this

last is known to be a perfectly transparent elastic fluid Whether the sulphurous oxide in this case is absorbed by the water in that state, or is gradually converted into sulphurous or sulphuric acid, I have not been able yet to determine

When a solution of sulphuret of lime has been exposed to the air for a few weeks, till it becomes colourless, and sulphur is no longer precipitated, if a little muriatic acid be added to it, the whole becomes milky, and exhales sulphurous acid, after some time sulphur is deposited, and the sulphurous acid vanishes, leaving muriate of lime in solution This milkiness must be occasioned by sulphurous oxide, for, sulphite of lime, treated in like manner, exhibits no such appearance

As far, then, as appears, sulphurous oxide is a compound of one atom of sulphur and one of oxygen, it is capable of combining with muriatic, and perhaps other acids, when suspended in water, it gives it a milky appearance and a bitter taste, and the mixture being heated, the oxide is changed into sulphur and sulphuric acid An atom of sulphur being estimated, from other considerations hereafter to be mentioned, to weigh 13, and one of oxygen weighing 7, it will follow that oxide of sulphur is constituted of 65 sulphur and 35 oxygen per cent

2 Sulphurous Acid

When sulphur is heated to a certain degree in the open air, it takes fire and burns with a blue flame, producing by its combination with oxygen an elastic fluid of a well known and highly suffocating odour, the fluid is called *sulphurous acid*. Large quantities of this acid are produced by the combustion of sulphur in close chambers, for the purpose of bleaching or whitening flannels and other woollen goods. In this way, however, the acid never constitutes more than 4 or 5 per cent of the volume of air, and is therefore much too dilute for chemical investigations. It may be obtained nearly pure by the following process. To two parts of mercury by weight put one part of concentrated sulphuric acid in a retort, apply the heat of a lamp, and sulphurous acid gas will be produced, which may be received over mercury. The reason of this is, each atom of mercury receives an atom of oxygen from one of sulphuric acid, and the remainder of the sulphuric atom constitutes one of sulphurous acid, as will be evident from what follows.

Sulphurous acid is unfit for respiration and for combustion its specific gravity, according

to Bergman and Lavoisier, is 205, according to Kirwan, 224, by my own trials, it is 23 I sent a stream of the gas, after it had passed through a cold vessel connected with the retort, into a flask of common air, this was afterwards weighed, and the quantity of acid gas then ascertained by water, it appeared by two trials, agreeing with each other, that 12 ounce measures of the gas weighed 9 grains more than the same quantity of common air, and this last weighed 7 grains nearly — Water absorbs about 20 times its bulk of this gas at a mean temperature, according to my experience, but some say more, others less The quantity absorbed, no doubt, will be greater as the temperature is less Hence, it seems that water has a chemical affinity for the gas, but the whole of it escapes if long exposed to the air, except a small portion which is converted into sulphuric acid

When water, impregnated with sulphurous acid, is exposed to oxygen in a tube, the oxygen is slowly imbibed, and sulphuric acid formed In twelve days, 150 measures of the acid, absorbed by water, took 35 of oxygen, leaving a residuum of oxygen and sulphurous acid When sulphurous acid gas and oxygen gas are mixed and electrified for an hour over mercury, sulphuric acid is formed, but I do

not find that the proportion of the elements of the acids can in this way be ascertained, for, the mercury becomes oxidized, and consequently liable to form an union with either of the acids — The two gases also combine, when made to pass through a red hot porcelain tube Sulphurous acid is said to be decomposed by hydrogen and charcoal at a red heat, sulphur is deposited, and water or carbonic acid formed, according as the case requires When a measure of oxymuriatic acid gas is put to a measure of sulphurous acid gas, over mercury, the sulphurous acid is converted into sulphuric, but no exact result can be obtained, from the rapid action of the former gas on mercury

Sulphurous acid oxidizes few of the metals, but it possesses the common properties of acids, and unites with the alkalies, earths, and metallic oxides, forming with them salts denominated *sulphites*

It remains now to investigate the number and weight of the elements in sulphurous acid I have made a great number of experiments on the combustion of sulphur in atmospheric air, in various circumstances, but those I more particularly rely upon, were made in a receiver containing 400 cubic inches it was open at top, and had a brass cap, by means of which an empty bladder could be attached to

the receiver, in order to receive the expanding air, a small stand was provided, and a watch glass was placed on it, filled with a known weight of the flowers of sulphur, the whole was placed on the shelf of a pneumatic trough, and as soon as the sulphur was lighted by an ignited body, the receiver was placed over it, with its margin in the water, the combustion was then continued till the blue flame expired. near the conclusion, white fumes arise copiously, and fill the receiver A small phial was then filled with water, inverted, and carefully pushed up into the receiver to withdraw a portion of air for examination, the receiver was then removed, and the loss of sulphur ascertained The residuary gas in the phial was fired with hydrogen in Volta's eudiometer The loss of sulphur at a medium was 7 grains, and the oxygen in the residuary gas was at a medium 16 per cent or rather more, the weight of oxygen, therefore, which had disappeared, was from 5 to 6 grains Hence it may be said, that 7 grains of sulphur combined with $5\frac{1}{2}$ of oxygen, but as the white fumes are oxidized inferior to sulphurous acid, it is most probable that sulphur requires its own weight of oxygen nearly to form sulphurous acid In confirmation of this, it is observable, that no material change of bulk is

effected in the gas by the combustion, and this is also remarked in the analogous combustion of charcoal. Thus, then, the specific gravity of sulphurous acid should exhibit a near approximation to twice that of oxygen, as it is found to do above. Now, as it would be contrary to all analogy, to suppose sulphurous acid to consist of 1 atom of sulphur and 1 of oxygen, we must presume upon its being 1 of sulphur and 2 of oxygen, and hence the weight of an atom of sulphur will be 14 times that of hydrogen.

Another and more rigid proof of the constitution of sulphurous acid, we obtain from the combustion of sulphuretted hydrogen in Volta's eudiometer. This compound, it will be shewn, contains exactly its own bulk of hydrogen, the rest is sulphur. Their relative weights, as appears from the specific gravity, must be 1 to 14 nearly, now, when sulphuretted hydrogen is exploded with plenty of oxygen over mercury, the whole of the last mentioned gas is converted into water and sulphurous acid, it is found that 2 measures of the combustible gas combine with 3 measures of oxygen, but 2 measures of hydrogen take 1 measure of oxygen, therefore, the sulphur takes the other 2 measures, that is, the atom of sulphur requires 2 atoms of oxygen for its

combustion, and that of hydrogen 1 atom of oxygen , which gives the same constitution as that deduced above for sulphurous acid

The proportions of sulphur and oxygen in this acid, have been variously stated, mostly wide of the truth We have one account that gives 85 sulphur and 15 oxygen Dr Thomson, in Nicholson's Journal, vol 6, page 97, gives 68 sulphur and 32 oxygen , but in his Appendix to the 3d edition of his Chemistry, he corrects the numbers to 53 sulphur and 47 oxygen. Desormes and Clement say 59 sulphur and 41 oxygen (*ibid* vol 17—page 42) According to the preceding conclusions, if the atom of sulphur be stated at 14 , then the proportion of sulphur to oxygen will be 50 sulphur to 50 oxygen, or equal weights , but if sulphur be denoted by 13, then sulphurous acid will consist of 48 sulphur and 52 oxygen per cent , which numbers I consider as the nearest approximation the diameter of the elastic atom of sulphurous acid is rather less than that of hydrogen, as appears from the circumstance that 5 measures of the gas saturate 6 measures of sulphuretted hydrogen which last contain as many atoms as the like measures of . . . On this account, the diameter of an atom of sulphurous acid may

be denoted by 95, and the number of atoms in a given volume, to that of hydrogen in the same volume, will be as 6 to 5, or 120 to 100.

3 *Sulphuric Acid*

The sulphuric acid of commerce, commonly known in this country by the name of *oil of vitriol*, is a transparent liquid of an unctuous feel, of the specific gravity 1.84, and very corrosive, it acts powerfully on animal and vegetable substances, destroying their texture, and mostly turning them black. This acid was formerly obtained from green vitriol (sulphate of iron) by distillation, hence the name *vitriolic acid*. It is now commonly obtained by burning sulphur, mixed with a portion of nitre, (from $\frac{1}{3}$ th to $\frac{1}{2}$ th of its weight) in leaden chambers, sulphuric acid is formed and drops down into water, which covers the floor of the chambers, this water, when charged sufficiently with acid, is drawn off, and subjected to evaporation till the acid is concentrated in a higher degree, when it is put into glass retorts, and placed in a sand bath, the weaker part of the acid is distilled into receivers, and the others concentrated nearly as much as is pos-

sible in the circumstances The acid in the receivers is again boiled down and treated as before

Some authors have affected to consider the theory of the formation of sulphuric acid as very obvious , the nitre, they say, furnishes a part of the oxygen to the sulphur, and the atmosphere supplies the rest Unfortunately for this explanation, the nitre, if it were all oxygen, would not furnish above $\frac{1}{4}$ -th of what is wanted , but nitre is only 35 per cent oxygen , it cannot, therefore, supply the sulphur with much more than $\frac{1}{8}$ -th part of what it wants, if all the oxygen were extricated , but not more than $\frac{1}{2}$ or $\frac{1}{3}$ d of this small portion is disengaged from the potash , for, the salt becomes a sulphate instead of a nitrate, and retains most of the oxygen it had, or acquires oxygen again from some source Several well informed manufacturers, aware of the fallacy of the above explanation, have attempted to diminish the nitre (which is an article of great expence to them), or to discard it altogether , but they find it indispensably necessary in some portion or other , for, without it they obtain little but sulphurous acid, which is in great part incondensable, and not the acid they want The manner in which the nitre operates, for a long time remained an ænigma At

length Desormes and Clement, two French chemists, have solved the difficulty, as may be seen in an excellent essay in the *Annales de Chimie*, 1806, or in Nicholson's *Journal*, vol. 17. These authors shew, that in the combustion of the usual mixture of sulphur and nitre, sulphurous acid is first formed, and nitrous acid or nitrous gas liberated, partly from the heat, and partly perhaps from the action of sulphurous acid, the nitrous gas or acid becomes the agent in oxidizing the sulphurous acid, by transporting the oxygen of the atmospheric air to it, and then leaving them in union, which constitutes sulphuric acid. The particle of nitrous gas then attaches another of oxygen to itself, and transports it to another atom of sulphurous acid, and so on till the whole is oxidized. Thus the nitrous acid operates like a ferment, and without it no sulphuric acid would be formed.

This theory of the formation of sulphuric acid has so very imposing an aspect, that it scarcely requires experiment to prove it. It is, however, very easily proved by a direct and elegant experiment. Let 100 measures of sulphurous acid be put into a dry tube over mercury, to which add 60 of oxygen, let then 10 or 20 measures of nitrous gas be added to the mixture in a few seconds the inside of

the tube becomes covered with a crystalline appearance, like hoar frost, and the mixture is reduced to $\frac{1}{3}$ d or $\frac{1}{4}$ th of its original volume If now a drop of water be admitted, the crystalline matter is quickly dissolved into the water, sparkling as it enters, and the gases entirely lose their elasticity, except a small residuum of azote and nitrous gas If the tube is then washed out, the water tastes strongly acid, but has no smell of sulphurous acid It is evident, that in this process the nitrous gas unites to the oxygen, and transports it to the sulphurous acid, which, receiving it from the nitrous, becomes sulphuric acid It appears, moreover, that solid sulphuric acid is formed when no water is present, and consequently this is the natural state of sulphuric acid entirely free from water It must be observed, that if any water in substance is present when the mixture of gases is made, the water seizes the nitrous acid as it is formed, and consequently prevents it oxidizing the sulphurous acid, on the other hand, the presence of water seems necessary in the sequel, to take the new formed sulphuric acid away, in order to facilitate the oxidizement of the remaining sulphurous acid The oxygen necessary to saturate 100 measures of sulphurous acid seems to be about 50 measures, but it is difficult to

ascertain this with precision, because the nitrous gas takes up the superfluous oxygen, and begins to act upon the mercury

Now, it has been shewn, that sulphurous acid contains nearly its own bulk of oxygen, and is constituted of 1 atom of sulphur and 2 of oxygen, and it appears from the above, that half as much oxygen more, that is, 1 atom, converts it into sulphuric acid hence, the sulphuric acid atom is constituted of 1 atom of sulphur and 3 of oxygen , and if the atom of sulphur be estimated at 13 in weight, and the 3 of oxygen at 21, the whole compound atom will weigh 34 times the weight of an atom of hydrogen , that is, pure sulphuric acid consists of 38 sulphur and 62 oxygen per cent

In the year 1806, by a careful comparison of all the sulphates, the proportions of which are well known, I deduced the weight of the atom of sulphuric acid to be 34 , it now appears that the same weight is obtained synthetically, or without any reference to its combinations , the perfect agreement of these deductions, renders it beyond doubt that the weight is nearly approximated, and confirms the composition of the atom which has just been stated

There are scarcely any chemical principles

the proportions of which have been so diversely determined by experimentalists, as those of sulphuric acid the following table will sufficiently prove the observation, according to

Berthollet	72	sulphur + 28 oxygen
Tromsdorf	70	_____ + 30 _____
Lavoisier	69	_____ + 31 _____
Chenevix	61 5	_____ + 38 5 _____
Thenard	55 6	_____ + 44 4 _____
Bucholz	42 5	_____ + 57 5 _____
Richter	42	_____ + 58 _____
Klaproth	42	_____ + 58 _____

Chenevix's result would have been 44 sulphur + 56 oxygen, if he had adopted 33 per cent acid in sulphate of barytes, which is now generally admitted. The method which he and the later experimentalists have taken, is to distil nitric acid from a given weight of sulphur, till the whole or some determined part of the sulphur is converted into sulphuric acid, the acid is then saturated with barytes, and the weight of the salt ascertained.

Notwithstanding the above theory of the formation of sulphuric acid was such as to convince me of its accuracy, I was desirous to see the manufacture of it on a large scale

and by the generous invitation of Mr Watkins, of Darcy Lever, near Bolton, I had lately an opportunity of gratifying myself by the inspection of his large and well-conducted acid manufactory, near that place When opening a small door of the leaden chambers, there issued a volume of red fumes into the air, which by their colour and smell, left no room to doubt of their being the fumes of nitrous acid There was scarcely any smell of sulphurous acid From the nitrous fumes, one would have been inclined to think that the chambers were filled with nitrous gas I was particularly anxious to know the constitution of the air in the interior of the chambers, and Mr Watkins was so obliging as to send me a number of phials of air taken from thence Upon examination, the air was found to consist of 16 per cent oxygen and 84 azote There was no smell of sulphurous acid, and very little of nitrous acid, this last having been condensed in passing through the water In fact, it seems that the nitrous acid fumes never make more, perhaps, than 1 per cent upon the whole volume of air , nor can the oxygen be ever reduced much below 16 per cent , because the combustion would instantly cease A constant dropping is observed from the roof of the chambers internally , these drops

being collected, were found to be of the specific gravity 1 6 , they had no sulphurous smell, but one slightly nitrous

It is not very easy to suggest any plausible alteration in the management of a manufactory of this article — Nitrous acid must be present, but whether it is best obtained by exposing nitre to the burning sulphur, or by throwing in the vapour of nitrous acid by direct distillation, may be worth enquiry Loss of nitrous acid is unavoidable, partly by its escape into the air during the periods of ventilation, and partly by its condensation in the watery acid, on the floors of the chambers, a regular supply must, therefore, be provided, but if this exceed a certain quantity, it not only increases the expence, but is injurious to the sulphuric acid in some of its applications There must, in all probability, be some figure of the chambers better than any other, in regard to their proportions as to length, breadth, and height, this, perhaps, can be determined only by experience As water absorbs the nitrous acid with avidity, high chambers, and the combustion carried on at a distance from the water, must be circumstances favourable to economy in regard to nitre

Sulphuric acid has a strong attraction for water, it even takes it from the atmosphere

in the state of steam, with great avidity, and is therefore frequently used in chemistry for what is called *drying* the air. When mixed with water, sulphuric acid produces much heat, as has already been stated in the first part of this work.

When sulphuric acid is boiled upon sulphur, it has been said sulphurous acid is formed. I have not found this to be the case. But charcoal and phosphorus decompose the acid by heat, and the results are carbonic acid, phosphoric acid, and sulphurous acid.

Sulphuric acid combines with the alkalies and earths in general, forming with them salts denominated *sulphates*. On the metals this acid acts variously, according to its concentration, when diluted with 5 or 6 times its bulk of water, it acts violently on iron and zinc, great quantities of hydrogen gas are produced, which proceed from the decomposition of the water, and the oxygen of the water unites with the metal, to which the acid also joins itself, and a sulphate is thus formed. When the acid is concentrated, its action on metals is less violent, but by the assistance of heat, it oxidizes most of them, and gives off sulphurous acid.

As the sulphuric acid exists in various degrees of concentration, it becomes a matter of

importance both to its manufacturer, and to those who use it largely, as the dyers and bleachers, to know the exact strength of it; or in other words, to know how much water is combined with the pure acid in any specimen. This subject engaged the particular attention of Kirwan some years ago, and he has furnished us with a table of the strengths of sulphuric acid, of most densities. There are two things requisite to form an accurate table, the one is to ascertain the exact quantity of real acid in some specimen of a given specific gravity, the other is to observe carefully the effects produced on the specific gravity of such acid, by diluting it with a given quantity of water. Mr Kirwan has succeeded very well in the former, but has been peculiarly unfortunate in the latter. The errors of his table seem to have been known for the last 10 years to every one, except the editors of works on chemistry. The following table exhibits the results of my own experience on this acid for several years.

Table of the quantity of real acid in 100 parts of liquid sulphuric acid, at the temperature 60°

Atoms Acid. Water	Acid per cent by weight	Acid per cent by measure	Specific gra- vity	Boiling point
1 + 0	100	unknown	unknown	unknown
1 + 1	81	150	1 850	620°
	80	148	1 849	605°
	79	146	1 848	590°
	78	144	1 847	575°
	77	142	1 845	560°
	76	140	1 842	545°
	75	138	1 838	530°
	74	135	1 833	515°
	73	133	1 827	501°
	72	131	1 819	487°
	71	129	1 810	473°
	70	126	1 801	460°
	69	124	1 791	447°
1 + 2	68	121	1 780	435°
	67	118	1 769	422°
	66	116	1 757	410°
	65	113	1 744	400°
	64	111	1 730	391°
	63	108	1 715	382°
	62	105	1 699	374°
	61	103	1 684	367°
	60	100	1 670	360°
1 + 3	58 6	97	1 650	350°
	50	76	1 520	290°
	40	56	1 408	260°
1 + 10	30	39	1 30+	240°
1 + 17	20	24	1 200	224°
1 + 38	10	11	1 10—	218°

Remarks on the preceding Table

1 The acid of 81 per cent. is constituted of 1 atom of acid and 1 of water It is the strongest possible acid that can be obtained by boiling the liquid acid, because at that strength

the acid and water distil together, in the same way as nitric acid of 1 42 sp gravity, or muriatic of 1 094 It is a mistaken notion, that the common sulphuric acid of commerce is of the maximum strength, though it is of the maximum density nearly The fact is, acid nearly of the maximum strength varies very little in its specific gravity, by the addition or subtraction of a small quantity of water Here is Kirwan's principal error Acids of the strength of 81 and 80, do not differ more than 1 in the third place of decimals , whereas, according to his table, the difference is 14 times as great The acid of commerce varies from 75 to 80 per cent of acid, or about 7 per cent in value, in the different specimens I have had occasion to examine This variation only changes the second figure in decimals an unit , though, according to Kirwan's table, the change is 7 times as much The specific gravity ought not to be the criterion of strength in acids above 70 per cent , the temperature at which they boil is a much better criterion, because it admits of a range of 12 or 15° for 1 per cent of acid Or the strength may be found by determining what quantity of water must be added to reduce the acid to some known strength, as that of the glacial acid of 1 78 sp gravity

2 There is nothing further striking in the table till we come to the acid, which is constituted of 1 atom to 2 of water, this acid possesses the remarkable property of congealing in a temperature at or above 32° , and of remaining congealed in any temperature below 46° , its specific gravity is 1 78, as Keir found it, (Philos Trans 1787), and it contains 68 per cent of real acid, both by theory and experiment, it is determined by theory thus — one atom of sulphuric acid weighs 34, and 2 of water 16, together making 50, hence, if $50 - 34 = 100 - 68$, it is found experimentally thus let 100 grain measures of glacial sulphuric acid be saturated with carbonate of potash, and the sulphate of potash be obtained, it will weigh, after being heated to a moderate red, nearly 270 grains, of which 121 will be acid, and 149 alkali, according to the analyses of Kuwan and Wenzel If the liquid acid be of greater or less specific gravity, so as to contain even 1 per cent more or less real acid, then it cannot be frozen in a temperature above 32° , but may in a temperature a little below 32° If the liquid acid contain 3 per cent more or less than the glacial, it cannot be frozen without the cold produced by a mixture of snow and salt, and

per cent from the glacial, as Mr Keir determined I find the frozen acid to be of the specific gravity 1 88 nearly It seems probable that the difficulty of freezing would increase in both sides, till the acids of 1 and 1 above, and 1 and 3 below

3 The acids below 30 per cent may, without any material error, have their strength estimated by the first and second figures of decimals in the column of sp gravity, thus acid of 15 per cent strength, will have the specific gravity 1 15, &c

SECTION 5

OXYGEN WITH PHOSPHORUS

There are only two compounds of oxygen and phosphorus yet known they both have the characters of acids, the one is denominated phosphorous acid, the other phosphoric acid It is extremely probable that the former, though recognised as an acid, is yet in the lowest degree of oxidation, and may therefore with equal propriety be called *phosphorous oxide*, *phosphoric oxide*, or, after the manner of metals, *oxide of phosphorus* We shall, however, adopt the common name

1 *Phosphorous Acid*

When phosphorus is exposed for some days to the atmosphere, it gradually acquires oxygen, and is converted into an acid liquid. This process may be effected by putting small pieces of phosphorus on the sloping sides of a glass funnel, and suffering the liquid to drop into a phial as it is formed. The liquid, called phosphorous acid, is viscous, tastes sour, and is capable of being diluted with water to any amount. It has the usual effect of acids on the test colours. When heated, water is evaporated, and afterwards phosphuretted hydrogen gas, finally, there remains phosphoric acid in the vessel. It should seem from this, that heat gives the oxygen of one part of the phosphorous acid to another, by which the latter is changed into phosphoric acid, and the phosphorus of the former is liberated, but at that degree of heat the liberated phosphorus acts on the water, one part of it takes the oxygen to form more phosphorous acid, and the other takes the hydrogen to form phosphuretted hydrogen, and thus the process is carried on till all the phosphorus is in the state of phosphoric acid, or phosphuretted hydrogen. It is probable that in this way the phosphorus

is divided, so that two thirds of it are united to oxygen, and one third to hydrogen, but this has not been ascertained by direct experiment

Phosphorous acid acts upon several metals, oxidizing them by the decomposition of water, and at the same time giving out phosphuretted hydrogen, the resulting metallic salts are, it is supposed, phosphates, the redundant phosphorus being carried off by the hydrogen This acid combines with the alkalies, earths, and metallic oxides, and forms with them a class of salts called *phosphutes*

When nitric acid is put to phosphorous acid, and heat applied, the nitric acid is decomposed, half of its oxygen unites to the phosphorous acid, and converts it into phosphoric acid, and the rest of the nitric acid escapes in the form of nitrous gas

The proportion of the two elements constituting phosphorous acid has not hitherto been ascertained, I am inclined to believe, from the experiments and observations about to be related concerning phosphoric acid, that phosphorous acid is composed of 1 atom of phosphorus, weighing 9 nearly, and 1 or oxygen, weighing 7, the compound weighing 16 If this be the case, it may appear singular that none of the other elements exhibit acid pro-

perties when combined with 1 atom of oxygen , but it should be observed, that the phosphoric oxide is in a liquid form, and disposed to separate into phosphorus and phosphoric acid, circumstances that do not combine in regard to the other oxides In fact, phosphorous acid may be considered as phosphoric acid holding phosphorus in solution, rather than as a distinct acid

2 Phosphoric Acid

Though some of the compounds of phosphoric acid, and the earths and alkalies, are common enough, yet this acid, in a pure state, is rarely obtained in any considerable quantity, requiring a process both tedious and expensive There are three methods by which phosphoric acid may be formed 1 If a small portion of phosphorus, namely, from 5 to 20 grains, be ignited, and immediately covered with a large bell glass, over water, the phosphorus burns with great brilliancy, and soon fills the vessel with white fumes , in a short time, the combustion ceases , after which the fumes gradually subside, or adhere to the side of the glass in the form of dew , these white fumes are pure phosphoric acid 2 If a small

piece of phosphorus be dropped into heated nitric acid in a phial or gas bottle, a brisk effervescence ensues, occasioned by the escape of nitrous gas, and the phosphorus gradually disappears, being converted into phosphoric acid, and mixed with the remaining nitric acid, another small piece may then be dropped into the liquid, and so on in succession till the nitric acid is almost wholly decomposed, the remaining liquid may then be gradually increased in temperature, to drive off all the nitric acid, what is left is a liquid consisting of phosphoric acid and water, by increasing the heat to a moderate red, the water is driven off, and liquid phosphoric acid remains, which on cooling becomes like glass 3 If phosphorous acid be prepared by the slow combustion of phosphorus, as mentioned above, and then a portion of nitric acid added to the liquid, and heat be applied, the nitric acid gives part of its oxygen to the phosphorous acid, and nitrous gas escapes What remains, when heated, is pure phosphoric acid

Of these three processes, the first may be recommended when the object is to find the proportion of the elements of the acid, but the second and third, when the object is to procure a quantity of acid for the purposes of investigation Of these the third is preferable

in an economical point of view, because it requires only half as much nitric acid. By calculation, I find that 20 grains of phosphorus will require 200 grains of nitric acid of 1 35, by the second process, but only 100 grains by the third, but a small excess should always be allowed for loss by evaporation, &c.

Phosphoric acid, in the state of glass, is deliquescent when exposed to the air, it becomes oily, and may be diluted with any quantity of water. This acid is not so corrosive as some others, but it has the other acid properties of a sour taste, of reddening vegetable blues, and of combining with the alkalies, earths, and metallic oxides, to form salts, which are called *phosphates*. It has the power of oxidizing certain metals, by decomposing water in the manner of sulphuric acid, the oxygen of the water unites to the metal, and the hydrogen is liberated in the state of gas. Charcoal decomposes this acid, as well as the phosphorous, in a red heat, hence the process for obtaining phosphorus from super-phosphate of lime.

Nothing very certain has been determined respecting the relation of the strength of this acid to the specific gravity of the liquid solution. Some experience I have had, makes me

think the following table will be found nearly correct at all events, it may have its use till a better can be formed

**Table of the quantity of real acid in 100 parts
of liquid phosphoric acid**

Acid per cent by weight	Acid per cent by measure	Specific gravity
50	92 5	1 85
40	64	1 60
30	41 7	1 39
20	24 6	1 23
10	11	1 10

Lavoisier ascertained the relative weights of phosphorus and oxygen in phosphoric acid to be 40 to 60 nearly this was effected by burning phosphorus in oxygenous gas This important fact has been since corroborated by the experience of others I find a near approximation to this result by burning phosphorus in atmospheric air In a bell glass, containing 400 cubic inches of air, 5 grains of phosphorus were repeatedly burnt over water, the combustion at first was very vivid, but towards the conclusion it was languid, there was a residuum of moist, half burned phosphorus in the cup, usually about 1 grain the glass had a flaccid bladder adapted to it to receive the rarefied air, so as to suffer none to

escape The air at first contained $20\frac{1}{2}$ per cent oxygen , but after the combustion, it contained only 16 or $16\frac{1}{2}$ per cent , the temperature being about 40° at the time Whence, by calculation, it appears that in these instances 1 grains of phosphorus may be concluded to have united to 6 grains of oxygen The data, indeed, would give a rather less proportion of oxygen ; but it is probable that some phosphorous acid is formed near the conclusion of the combustion

With respect to the constitution of the phosphoric acid atom, there can be but two opinions entertained Either it must be 1 atom of phosphorus with 2 atoms of oxygen, or with 3 of oxygen According to the former opinion, the phosphoric atom will weigh 9, and the phosphoric acid atom 23 , according to the latter opinion, the phosphoric atom will weigh 11, and the acid atom 35 We might appeal to the phosphates to determine the weight of the acid , but this class of salts has not been analyzed with sufficient precision Fortunately, there is another compound of phosphorus which is subservient to our purpose , namely, phosphuretted hydrogen As the properties of this gas will be treated of in the proper place, we shall only observe here that the gas is a compound of phosphorus and

hydrogen, that it contains just its bulk of hydrogen, that its specific gravity is about 10 times that of hydrogen, and that when fired in Volta's eudiometer along with oxygen, it is converted into water and phosphoric acid, requiring 150 per cent in volume of oxygen for its complete combustion, but is, notwithstanding, burnt so far as to lose its elasticity with 100 measures of oxygen. These facts leave no doubt that the atom of phosphorus weighs 9, that the atom of phosphoric acid weighs 23, being a compound of 1 with 2 of oxygen, that the atom of phosphorous acid is 1 with 1 of oxygen, weighing 16, and that phosphorous acid and water are formed when equal volumes of phosphuretted hydrogen and oxygen are exploded together.

SECTION 6

HYDROGEN WITH AZOTF.

Only one compound of hydrogen and azote has yet been discovered. It has been long known to chemists as an important element, and under various names, according to the state in which it was exhibited, or to the article from which it was derived, namely, vo-

volatile alkali, hartshorn, spirit of sal ammoniac, &c but authors at present generally distinguish it by the name of *ammonia*. Its nature and properties we shall now describe.

Ammonia

In order to procure ammonia, let one ounce of powdered sal ammoniac be well mixed with two ounces of hydrate of lime (dry slaked lime), and the mixture be put into a gas bottle, apply the heat of a lamp or candle, and a gas comes over, which must be received in jars over dry mercury. It is *ammoniacal gas*, or ammonia in a pure state.

This gas is unfit for respiration, and for supporting combustion, it has an extremely pungent smell, but when diluted with common air, it forms an useful and well-known stimulant to prevent fainting. The specific gravity of this gas has been found nearly the same by various authors, which is the more remarkable, as the experiment is attended with some difficulties that do not occur in many other cases. According to Davy, 100 cubic inches of it weigh 18 grains, according to Kirwan, 18 2 grains, Allen and Pepys, 18 7, and Biot, 19 6, the mean of these, 18 6 grains.

may be considered as a near approximation at the temperature 60° and pressure 30 inches of mercury hence the specific gravity is 6, the weight of atmospheric air being one

Ammoniacal gas sent into water, is condensed almost with the same rapidity as steam, in this respect it corresponds with fluoric and muriatic acid gases The compound of water and ammonia forms the common liquid ammonia sold by the name of *spirit of sal ammoniac*, this is the form in which ammonia is the most frequently used It is of great importance to ascertain the quantity of gaseous or real ammonia in given solutions of ammonia in water This subject has been greatly neglected, a very good attempt was made about 10 years ago by Mr Davy, to ascertain the quantity of ammonia in watery solutions, of different specific gravities, the result was a table, which may be considered an excellent first approximation, but it is to be regretted that so important an enquiry should not have attracted attention since I have instituted a few experiments on this head, the results of which will no doubt be acceptable

A phial, capable of holding 1100 grains of water, was partly filled with mercury, and the rest with 200 grains of water, and inverted in mercury, into this 6000 grain measures of am-

moniacal gas were transferred, the liquid had not diminished sensibly in specific gravity; it required $24\frac{1}{2}$ grain measures of muriatic acid, 1 155, to saturate the water, by evaporating in a heat below boiling water, 12 grains of dry muriate of ammonia were obtained. Now, supposing 1400 measures of gas equal to 1 grain in weight, there would be found in the salt 5 7 grains of muriatic acid, 4 3 grains of ammonia, and 2 grains of water. I found this method of proceeding not to be relied upon, for, though the mercury had recently been dried in an oven in the temperature 240°, yet the ammoniacal gas could not be transferred from one graduated tube to another, without a loss of 10 or 15 per cent, I had reason to conclude, then, that the ammonia in the above salt was overrated. In order to avoid this source of error, I adopted the method first used by Dr Priestley, of putting muriatic acid gas to the alkaline in the graduated tube, but here was still an objection, as the muriatic acid gas must be measured previously to the transfer, and it is equally absorbable by water with alkaline gas. However, I found, as Dr Priestley had done before, that equal measures of the two gases as nearly as possible saturated each other. For, when a measure of acid gas was put to one of alkaline, there was a small

residuum of alkaline gas , and when the alkaline was transferred to the acid, there was a small residuum of acid gas Having before concluded (page 287) that muriatic acid gas was of the specific gravity 1 61, I might have adopted the ratio of acid and alkali in muriate of ammonia to be 1 61 to 6 , and hence have inferred the quantity and volume of ammonia in a given solution, from the quantity of muriatic acid solution requisite to saturate it But there was one important circumstance against this , the atom of muriatic acid I knew weighed 22, and the ratio of 1 61 to 6, is the same as 22 to 8 2 nearly , hence, the weight of an atom of ammonia must have been 8 2 or 4 1, which I was aware was inconsistent with the previous determinations concerning azote and hydrogen Observing in the 2d vol of of the *Mémoires d'Arcueil*, that Biot and Gay Lussac find the specific gravity of muriatic acid gas to be so low as 1 278, and understanding from conversation with Mr Davy, that he also had found the specific gravity of the gas to be considerably less than I had concluded, I was induced to repeat the experiment of weighing it, taking every care to avoid the introduction of liquid solution I sent a stream of acid gas, derived from common salt and concentrated sulphuric acid,

through an intermediate vessel, into a dry flask of common air, loosely corked, till it had expelled $\frac{3}{4}$ ths of the air, as appeared afterwards, the inside of the glass had a very slight opacity on its surface, it had gained $1\frac{1}{10}$ grain in weight, it was then uncorked and its mouth plunged into water, when $\frac{3}{4}$ ths of the flask were in a few moments occupied by the water Other trials gave similar results The flask held 6 grains of common air Whence I derive the specific gravity of muriatic acid gas to be 1 23, and am induced to apprehend that this is rather more than less than the truth The weights of equal volumes of muriatic acid gas and ammoniacal gas will then be as 1 23 to .6, or as 22 to 11, nearly, and if we assume that 11 measures of acid gas are sufficient for 12 of alkaline, which is not unlikely from experience, then we shall have 22 parts acid to 12 of ammonia for the constitution of muriate of ammonia (exclusive of water), which will make the theory and experience harmonize, according to this view, muriate of ammonia must consist of 1 atom of muriatic acid and 2 of ammonia, each atom of ammonia being a compound of 1 atom of azote and 1 of hydrogen However this may be, I find that 22 parts of real muriatic acid, 38 of nitric, and 34 of sulphuric, as determined by the re-

spective foregoing tables, will saturate equal portions of any ammoniacal solution, these, then, may be considered as tests of the quantity of real ammonia in different solutions, and if the ratio of 22 to 12, above adopted, be incorrect, it cannot be greatly so, and the error will be general, being so much per cent upon any table of ammoniacal solutions. The test acids I prefer for use, are such as contain half the quantities of acid above stated in 100 grain measures. Thus, 100 grain measures of muriatic acid, sp. gravity 1 074, contain 11 grains of real acid, 100 measures of nitric acid, 1 141, contain 19 grains, and 100 measures of sulphuric acid, 1 135, contain 17 grains of real acid. Now, 100 measures of ammoniacal solution of 97 sp. gravity, are just sufficient to saturate these. Whence I adopt that solution as test ammonia, and conclude that 100 grain measures of it contain 6 grains of real ammonia.

It will be perceived, then, that the accuracy of the ensuing table depends upon several points namely, whether 100 measures of muriatic acid of 1 074, really contain 11 grains of acid, whether the specific gravities of muriatic acid gas, and ammoniacal gas, are really 1 23 and 6, or in that ratio, and whether 11 measures of acid gas saturate 12 measures of

ammoniacal gas I believe the errors in any of these particulars to be very small, and probably they may be such as partly to correct each other

I find, after Mr Davy, that a measure of water being put to a measure of ammoniacal solution, the two occupy two measures, without any sensible condensation, consequently, if the quantity of ammonia in a measure of any given specific gravity, as 90, be determined, then the quantity in a measure of 95, will be just half as much Hence, a table is easily constructed for measures, and one for weights is derivable without much calculation

Table of the quantities of real or gaseous ammonia in solutions of different specific gravities

Specific gravity	Grains of ammonia in 100 water grain measures of liquid	Grains of ammonia in 100 grains of liquid	Boiling point of the liquid old scale	Volume of gas condensed in a given volume of liquid
90	50	35 3	26°	494
89	28	32 6	38°	456
87	20	29 9	50°	419
88	24	27 3	62°	382
89	22	24 7	74°	346
90	20	22 2	86°	311
91	18	19 8	98°	277
92	16	17 4	110°	244
93	14	15 1	122°	211
94	12	12 8	134°	180
95	10	10 5	146°	147
96	8	8 3	158°	116
97	6	6 2	173°	87
98	4	4 1	187°	57
99	2	2	196°	28

On the above table, it may be proper to remark, that I have not had large quantities of ammoniacal solution lower than 94, so as to find their specific gravities experimentally; but have had small quantities to the amount of 10 or 20 grains of the several solutions from 26 to 12 per cent, I have no reason to suspect any material deviation from the law of descent observed in the specific gravity down to 12 per cent, when we go below that number, at all events, it cannot be great down to 85, and it is not of much importance, because solutions of that strength are never obtained in the large way — The second column, exhibiting the grains of ammonia in 100 measures of the solution, is more convenient for practice than the third, which gives the weight in 100 grains of solution The fourth column, which shews the temperature at which the several solutions boil, will be found highly interesting The ebullition of a liquid is well known to take place, when the steam or vapour from it is of the same force as the atmospheric pressure In solutions down to 12 per cent, the experiments were performed by inserting a thermometer into a phial containing the solution, and plunging the phial into hot water till the liquid boiled; but in the higher solutions a small portion, as 20

grains, was thrown up a tube filled with mercury , the tube was then put into a phial of mercury, and the whole plunged into warm water , the temperature was then ascertained requisite to bring the mercury in the tube to the level of that in the phial The fifth column is calculated from the second, supposing the specific gravity of ammoniacal gas = 6

It may be observed, that the above table gives the quantity of ammonia in different solutions, from 15 to 20 per cent less than Mr Davy's table , also, that the common ammoniacal solutions of the shops usually contain from 6 to 12 per cent of ammonia

Before we can estimate the value of the fourth and fifth columns of the table, we must ascertain the force of vapour from ammoniacal solutions at different temperatures If it be found in some one instance, we may by analogy infer the results in others As the steam from water varies in force in geometrical progression to equal increments of temperature, it might be expected that the steam or gas from liquid ammonia should do the same , but as the liquid is a compound, the simple law of the force of aqueous steam does not obtain It appears, however, from the following results, that a near approximation to this law is

observed Into a syphon barometer I threw a quantity of .946 liquid ammonia, which was by agitation, &c transferred to the vacuum over the mercury The vacuum was then immersed successively in water of different temperatures, and the force of the gas observed as under.

Temperature

old scale	new scale	differences	Force of ammoniacal steam from liquid 946
140°	151°		30 inch.
		36°	
103°	115°		15
		31°	
74°	84°		7 5
		29°	
50°	55°		3 75

Hence it seems, that the intervals of temperature required to double the force of ammoniacal steam, increase in ascending I had no doubt but this sort of steam or gas, would mix with common air, without having its elasticity affected, like as other steams do , but I ascertained the fact by experiment Thus I mixed a given volume of air with steam of 15 inches force, and found that the air was doubled in bulk

These facts are curious and important They shew that ammonia is not retained in water

without external force, and that the pressure of no elastic fluid avails but that of ammoniacal gas itself, thus establishing the truth of the general law which I have so much insisted on, that *no elastic fluid is a sufficient barrier against the passage of another elastic fluid*

We may now see upon what causes the saturation of water with ammonia depends. They are two, the *temperature* of the liquid, and the *pressure* of the incumbent ammoniacal gas, exclusive of the air intermixed with it. For instance, if the temperature be given, 50° (old scale); then the strongest possible solution, under atmospheric pressure, will be such, that 100 measures will have the specific gravity 87, and contain 26 grains of ammonia, or 419 times the volume of gas. But if, in saturating the water by sending up gas, there be common air, so as to make $\frac{4}{7}$ ths of the incumbent gas, then the solution cannot be made stronger than 946, of which 100 measures contain 11 grains of ammonia, or 162 times the volume of gas. I have obtained a saturated solution containing 26 per cent. ammonia, with $\frac{1}{72}$ th common air in the incumbent gas, and at the same temperature, another saturated solution, containing only 17 per cent ammonia, with $\frac{3}{4}$ ths common air in the incumbent gas.

With respect to the constitution of ammonia, Priestley, Scheele and Bergman pointed out the two elements into which it is decomposed Berthollet first settled the proportions of the elements, and the quantity of each obtained from a given volume of ammoniacal gas It is highly to his credit too, that subsequent repetitions of his experiments, under the improved state of knowledge, have scarcely amended his results Priestley resolved 1 measure of ammoniacal gas, by electricity, into 3 measures of gas not absorbable by water , but his ammonia could not have been dry Berthollet resolved 17 measures into 33 in the same way this result has since been corroborated by various authors He also found that the gas so produced, was a mixture of 121 parts of azote by weight, with 29 of hydrogen , or 4 \AA azote with 1 of hydrogen

In 1800, Mr Davy published his researches, in which were given several interesting results on ammonia, Mr Davy decomposed ammonia, by sending the gas through a red hot porcelain tube , after the common air was expelled, the collected gas was found free from oxygen To 140 measures of this gas were added 120 of oxygen , the mixture being exploded by electricity, 110 measures of gas were left and of course 150 were converted int

water, of this 100 measures must have been hydrogen Whence, 140 measures of the gas from decomposed ammonia, contained 100 hydrogen and 40 azote , or 100 measures contained 71 4 hydrogen and 28 6 azote This conclusion was so nearly agreeing with the previous determination of Berthollet, that both have justly been held up as specimens of the accuracy of modern chemical analysis

In 1808, Mr Davy published his celebrated discoveries relating to the decomposition of the fixed alkalies Having ascertained that these contained oxygen, he was led by analogy to suspect the same element in ammonia Several experiments were made, which seemed to countenance this idea , but these could not be considered conclusive, as long as it was admitted that no oxygen appeared in the decomposition of ammonia by electricity, and yet that the weight of the azote and hydrogen were together equal to that of the ammonia decomposed Mr Davy re-examined the specific gravity of ammoniacal gas, the quantity of gases evolved by the decomposition of a given volume of it, and the ratio of azote to hydrogen in the same The result was, that the gases obtained amounted only to $\frac{1}{4}$ ths of the weight of the ammonia , the remaining $\frac{3}{4}$ th Mr Davy thought must be oxygen,

which, uniting to hydrogen, formed a portion of water The way in which this part was saved, was principally by diminishing the absolute quantity of gases derived from a given volume of ammonia, but partly by finding less azote and more hydrogen than had been before estimated Thus, 100 measures of ammoniacal gas produced only 180 measures of mixed gas, though commonly estimated at 200, and this gas was found to consist of 26 azote and 74 hydroger per cent

These conclusions, so different from what had been long adopted, and depending upon experiments of some delicacy, were not likely to be received without a more general scrutiny Dr Henry in England, and A B Berthollet in France, seem both to have renewed the investigation into the component parts of ammonia with great care and assiduity Dr Henry's object was to determine whether any oxygen, water, or any other compound containing oxygen, could be detected in the analysis of ammonia , this enquiry included the two others, namely, the quantity of gases obtained from a given volume of ammoniacal gas, and the proportion of azote to hydrogen in the same The results were, that neither oxygen nor water could be found , that for the most part the bulk of ammonia was doubled

by decomposition, even when the gas was previously dried with extreme care , and that the ratio of azote to hydrogen in the mixture, from an average of six careful experiments, was $27\frac{1}{4}$ to $72\frac{3}{4}$. In this last decision, Dr Henry was so fortunate as to discover a more easy and expeditious mode of analysis than had been known before , he found that ammoniacal gas mixed with a due proportion of oxygen, of nitrous oxide, or even of nitrous gas, would explode by an electric spark He found an under proportion of oxygen gas to answer best (about 6 measures of oxygen to 10 of ammonia) the explosion produced a complete decomposition of the ammonia, and a partial combustion of the hydrogen , after which more oxygen was put to the residuum, and the remainder of the hydrogen consumed From one experiment, in which 100 measures of ammonia were decomposed in a tube of which the mercury had been previously boiled, Dr Henry only obtained 181 measures of gas , and he seems to think that this experiment may be the most correct in regard to that object (Philos Trans 1809)

In the Memoires d'Arcueil, tom 2, M A B Berthollet has a paper on the analysis of ammonia He alludes to the experiments of Berthollet in the memoirs of the academy

1785, in which the ratio of 27 5 azote to 72 5 hydrogen, was found in the decomposed ammonia, allowing 196 hydrogen for 100 oxygen He reports several experiments and observations relative to the oxidation and deoxidation of iron in ammoniacal gas He then proceeds to prove, that the weight of azote and hydrogen produced in the decomposition of ammonia, is equal to the weight of the ammonia itself Biot and Arago determine the specific gravities of azote, hydrogen, and ammonia, to be 969, 078, and 597 respectively, which A B Berthollet adopts He finds that 100 measures of ammonia produce 205 of permanent gas, which, by analysis, gives 24 5 azote and 75 5 hydrogen per cent Like Dr Henry, A B Berthollet decomposed ammonia by exploding it with oxygen gas, but unfortunately he used an excess of oxygen, and then determined the residuary oxygen by the addition of hydrogen he was aware, however, that part of the azote was thus converted into nitric acid Upon collecting the results, he makes it appear, that the gases produced by the decomposition of ammonia are, as nearly as possible, equal to the weight of the ammonia

Though the experiments of these two authors may be deemed satisfactory, with regard to the non-existence of oxygen in ammonia,

they would have been more so if they had accorded in the quantity of gas derived from a given volume of ammonia, and in the ratio of azote to hydrogen Having made some experiments myself on these heads, I may be allowed to give my opinion as to the causes of these differences —I am persuaded, with Mr. Davy, that ammonia is not doubled by decomposition, when due care is taken to prevent any liquid from adhering to the tube or mercury , but at the same time am inclined to believe, from experience, that 100 measures of ammonia will give not less than 185 or 190 measures of gas by dscomposition I took a tube and filled it with dried mercury , then transferred a portion of gas into it, and by pushing a glass rod up the tube several times, displaced the mercury in the tube, so that no liquid ammonia could exist in the renovated mercury This gas, being decomposed by electricity, produced after the rate of 187 for 100 With respect to the ratio of azote to hydrogen, I am convinced it is to be obtained only by decomposing the ammonia previously to the combustion of the hydrogen, and this may be done either by electricity or by heat , in these cases, ammonia will be resolved into 28 measures of azotic gas, and 72 measures of hydrogen gas in the hundred I have re-

peatedly obtained it so by electricity, the results never deviating farther than from 27 to 29 of azote This agrees sufficiently with Berthollet's original analysis by electricity, and with Davy's analysis by heat in 1800, both of them made without any theoretic views as to quantity, which cannot be said of any of the subsequent investigations on this subject

We are now to see how far these results will agree with the specific gravity of ammoniacal gas that is, whether the weights of the two gases are equal to the weight of the ammonia decomposed

Grains
100 measures of ammonia, which \times sp gr 6 gives 60
become 185 measures of mixed gas,
namely, 51 8 azote, — — — which \times sp gr 967 gives 50 09
and 133 2 hydrogen, — — — which \times sp gr 08 gives 10 65
<u>60 74</u>

The excess of $\frac{3}{4}$ ths of a grain upon 60, is too small to merit notice, and may arise from an inaccuracy in any of the data, which, if corrected, could have no material influence on the conclusions

I shall now make a few observations on the other methods of analyzing ammonia Dr. Henry's methods of burning ammonia in Volta's eudiometer along with oxyrogenous gas

nitrous gas, and nitrous oxide, unite elegance with expedition, and when well understood, cannot but be valuable It appears to me, however, both from experience and analogy, that a compound combustible, such as ammonia, is never decomposed and one of its elements burnt, to the entire exclusion of the other Numerous instances may be found in the compounds of charcoal and hydrogen, of phosphorus and hydrogen, &c where one of the elements seizes the oxygen with more rapidity than the other , but some portion of the other is always burnt Even when the combustible gases are only mixed together, and not combined, we do not find that one of them precludes the other from taking a share of the oxygen till it is saturated Thus, in a mixture of carbonic oxide with hydrogen, with a deficiency of oxygen, part of both is burnt by an electric spark Dr Henry has, indeed, noticed that ammonia fired with excess of oxygen, gives nitric acid as well as water I have reason to believe this is the case in some degree, in whatever proportion they are fired. I have seldom obtained so much as 27 per cent of azote by the combustion of ammonia with oxygen (the hydrogen being estimated by doubling the oxygen spent), and in no instance 28 but it will be manifest that all the

oxygen is not consumed in burning the hydrogen, if we note the ammoniacal gas expended, and allow only 66 or 67 per cent oxygen for the hydrogen, there will generally be found a greater expence of oxygen, which must have gone to form nitric acid The combustion of ammonia with nitrous gas usually gives from 25 to 27 per cent. of azote, allowing the constitution of nitrous gas to be what is stated at page 331 Upon the whole, I found nitrous oxide to approximate nearest to the truth When 100 measures of ammonia are exploded with 120 of nitrous oxide, the gases resulting are azote with a very small portion of hydrogen, if to this a little hydrogen be added, and then an excess of oxygen, another explosion will determine the residuary hydrogen, which being deducted, there remain about 172 azote, 120 of which come from the nitrous oxide, and 52 from the ammonia, which gives after the rate of 28 azote per cent on the evolved gases — When the decomposition of ammonia is attempted by oxymuriatic acid gas, a graduated tube is filled with the gas, and plunged into liquid ammonia in this way, if we reckon a measure of the acid gas to a measure of hydrogen, we shall find the azote evolved and left in the tube, amount to 23 or 24 per cent upon both gases It is to be presumed,

then, tha. oxymuriatic acid, like oxygen, consumes part of both the elements of ammonia

By comparing the weight of azote with that of hydrogen in the above table, we find them as 4 7 to 1 nearly This evidently marks the constitution of ammonia to be that of 1 atom of each of the elements combined But we have before determined the element of azote to weigh 5 1, when treating of the compounds of azote and oxygen This difference is probably to be ascribed to our having over-rated the specific gravity of nitrous gas, and perhaps nitrous oxide, In the *Mémoires d'Arcueil*, I observe Bérard finds the specific gravity of nitrous gas to be 1 04, instead of 1 10, which last I have made my calculations from , if the former should prove true, it will reduce my valuation of azote in nitric acid nearly to 4 7 , I have not had an opportunity of ascertaining the specific gravity of nitrous gas , but am inclined to believe that 1 10 may be too high Berthollet finds nitrous oxide to be 1 36, instead of 1 61 , I much suspect the former is too low

Upon the whole, we may conclude that an atom of ammonia is constituted of 1 atom of hydrogen and 1 of azote, and weighs nearly 6 The diameter of the elastic particle is 909,

that of hydrogen being 1 Or, 300 measures of ammoniacal gas contain as many atoms as 400 measures of hydrogen, or as 200 of oxygen

SECTION 7

HYDROGEN WITH CARBON

There are two combinations of hydrogen with carbone, now well known, easily distinguishable from each other and from all other combinations They are both elastic fluids, one of them, called olefiant gas, is a compound of 1 atom of hydrogen and 1 of carbone , the other, which I call carburetted hydrogen, is a compound of 2 atoms of hydrogen and 1 of carbone, as will be manifest from what follows

1 *Olefiant Gas*

The gas denominated *olefiant*, was discovered and examined by the Dutch chemists, Bondt, Dicman, &c and a memoir on the subject was published in the 15th vol of the Journal de Physique, 1791

Olefiant gas may be procured by mixing 2 measures of sulphuric acid with 1 measure of alcohol, this mixture in a gas bottle must be heated to about 300° by a lamp, when the liquid exhibits the appearance of ebullition, and the gas comes over. It should be passed through water, to absorb any sulphurous acid which may be generated

This gas is unfit for respiration, and extinguishes flame, but it is highly combustible its specific gravity, according to the Dutch chemists, is .905, according to Dr Henry, 967. Perhaps 95 is about the truth Water absorbs $\frac{1}{8}$ th of its bulk of this gas, or the atoms of gas in the water are just twice the distance they are without, and it may be expelled again by the other gases This property (of being absorbed by 8 times its bulk of water) occurred to me in 1804, in a course of experiments on the absorption of gases by water. It is peculiar to this gas, and consequently distinguishes it from all others When olefiant gas is mixed with oxymuriatic acid gas, a diminution takes place, like as when oxygen and nitrous gas are mixed, but the result is an oil, which swims on the surface of the water Hence the Dutch chemists gave this gas the name of *olefiant* For this purpose, they found 3 measures of olefiant gas required

4 measures of the acid gas, but Dr Henry finds 5 of olefiant require 6 of the acid. The difference is not great, considering the difficulty of the experiment. As neither of these results will agree with the other known properties of these two gases, I suspected that both would be found in some degree incorrect; which proved to be the case from the following experiments. Having taken two similar tubes graduated, containing each about 170 grains of water, I filled them, one immediately after the other, from a bottle generating oxymuriatic acid copiously, into one of these, 200 measures of olefiant gas were slowly transferred, after standing some time, the residuary gas was transferred and noted, then the other tube with acid gas was taken, the gas passed 5 or 6 times through water, till no further diminution was observed, and the residuary gas was noted and allowed for impurity in the first tube. By this procedure no acid gas was lost, and an excess of olefiant gas being used, the purity of this last did not enter into the calculation. In one trial, 165 measures of oxymuriatic acid gas condensed 168 of olefiant gas, in another, 165 took 167. From these, I conclude that oxymuriatic acid requires a very little more than its bulk of olefiant gas to be saturated perhaps 100 of the former may take

102 measures of the latter , but if we reckon equal volumes, the error cannot in general be material

Olefiant gas burns with a dense, white flame It explodes with uncommon violence when mixed with oxygen and electrified , the products resulting are various, according to the circumstances When completely saturated with oxygen, the results are, according to

	carb. acid.
Berthollet, 100 measures take 280 oxygen, produce 180	
Dr Henry, 100 — — 284 — — 179	

The rest of the produce is water These results, agreeing so well with each other, are the more plausible , but I can add that my own experience corroborates them, particularly in regard to oxygen My results have always given less than 300, but more than 270, the acid, I apprehend, should be about 185 or 190 unless a great excess of oxygen be used, the charcoal is partly thrown down, and it makes the gas turbid after the explosion , the result in this case affords less carbonic acid than is due

When olefiant gas alone is subjected to continued electricity, either over mercury or water, the result is hydrogen gas, and a quantity of charcoal is deposited A very careful experiment of this kind was made by Dr Henry

and myself, in which 42 measures of pure olefiant gas were electrified till they became 82, these were exploded with oxygen, and found to consist of 78 hydrogen, and 2 olefiant gas Here 40 olefiant became 78 hydrogen, or very near double The charcoal was thrown down According to this, 100 measures of olefiant gas will contain 195 of hydrogen, which require 98 oxygen for their combustion, now as the charcoal must take the rest, or nearly 196 measures, it follows that in the combustion of olefiant gas, 2 parts of the oxygen are spent upon the charcoal, and 1 part upon the hydrogen Hence we obtain this conclusion, that an atom of olefiant gas consists of 1 of charcoal and 1 of hydrogen united No oxygen can be present in olefiant gas, because during the elec rification it would be detected, either in the form of water or carbonic oxide

It will be proper now to see how far the weights of the gases entering into combination, agree with the previous determinations An atom of charcoal weighs .4 (see page 382), and 1 of hydiogen weighs 1, together making an atom of olefiant gas, .64 This atom will require 3 of oxygen for its combustion, namely, 2 for the charcoal, to form carbonic acid, and 1 for the hydrogen, to form water,

these 3 weigh 21, whence 6.4 parts of olefiant gas by weight, should take 21 of oxygen. Now supposing, according to Dr Henry's result, that 100 measures of olefiant gas require 284 for their combustion, and further, that the specific gravity of oxygenous gas is 1 10 (agreeably to Allen and Pepys, as also Biot and Arago), we shall have $284 \times 1 1 = 312 4$, the weight of the oxygen, hence, if 21 : 312 4 95, the weight of 100 measures of olefiant gas, corresponding to a specific gravity of 95. Hence, then, it appears that the weight of the gases combined, perfectly corroborates the above conclusions respecting the constitution of olefiant gas.

There are some remarkable circumstances attending the combustion of olefiant gas in Volta's eudiometer, which deserve notice as part of the history of the gas, but particularly as they put the constitution of the gas beyond all doubt. If 100 measures of oxygen be put to 100 of olefiant gas, and electrified, an explosion ensues, not very violent, but instead of a diminution, as usual, there is a great increase of gas, instead of 200 measures, there will be found about 360, some traces of carbonic acid are commonly observed, which disappear on passing two or three times through lime water, there will then remain, perhaps,

350 measures of permanent gas, which is all combustible, yielding by an additional dose of oxygen, carbonic acid and water, the same as if entirely burnt in the first instance. What, therefore, is this new gas in the intermediate state? The answer is clear. It is carbonic oxide and hydrogen mixed together, an equal number of atoms of each. One third of the oxygen requisite for the complete combustion, suffices to convert the carburetted hydrogen into carbonic oxide, and the hydrogen at the instant is liberated, hence the other two thirds are employed, the one to convert the carbonic oxide into acid, the other to convert the hydrogen into water. In fact, the 350 measures consist of nearly 170 of each gas, which together require nearly 170 of oxygen for their combustion *

* M Berthollet contends, that all the combustible gases into which carburetted hydrogen enter, contain also oxygen he calls them *oxycarburetted hydrogen*. Mr Murray also enters into his views in this respect — As far as relates to olefiant gas, it will be time enough for animadversion on this opinion, when the accuracy of the above facts and observations are questioned. But there is one circumstance which M Berthollet has not explained in regard to this gas, and it turns upon a point which he and I acknowledge, but which is not perhaps generally received, namely, that when two gases unite to form a third, this last is specifically heavier than the lighter of the two. Now, in the above

The diameter of an atom of olefiant gas is .81 to hydrogen 1 And 100 measures of it contain as many atoms as 188 of hydrogen, or as 94 of oxygen, or (probably) as 200 of oxy-muriatic acid , whence the union of this last with olefiant gas, must be 2 atoms of the gas with 1 of the acid

2 Carburetted Hydrogen

The gas which I denominate carburetted hydrogen, was known in a state of mixture, to Dr Priestley , he called all such mixtures by the name of *heavy inflammable air* La-voisier, Higgins, Austin, Cruickshanks, Berthollet, Henry and others, have since cultivated this department of science —Cruickshanks contributed much to unveil the subject, by pointing out carbonic oxide as an inflammable gas, *sui generis*, but often found mixed with other gases No correct notion of the constitution of the gas about to be described, seems to have been formed till the atomic

instance, we find olefiant gas and oxygenous gas, uniting to form a third (according to his opinion), which is lighter by one half nearly than the lighter of the two How is this new oxy carburetted hydrogen to be reconciled with the above principle ?

theory was introduced and applied in the investigation. It was in the summer of 1804, that I collected at various times, and in various places, the inflammable gas obtained from ponds, this gas I found always contained some traces of carbonic acid and a portion of azote, but that when cleared of these, it was of a uniform constitution. After due examination, I was convinced that just one half of the oxygen expended in its combustion, in Volta's eudiometer, was applied to the hydrogen, and the other half to the charcoal. This leading fact afforded a clue to its constitution.

Carburetted hydrogen gas may be obtained in a pure state, with the above exceptions, from certain ponds in warm weather. Clayey ponds, in the vicinity of a town, where soot and other carbonaceous matter is deposited, abound with this gas. The bottom of the pond being stirred with a stick, large bubbles ascend, which may be caught by filling a tumbler with water, and inverting it over the ascending bubbles. This gas is obtained nearly pure also by distilling pitcoal with a moderate red heat. It is now largely used as a substitute for lamps and candles, under the name of *coal gas*. According to Dr Henry's analysis, coal gas does not usually contain more than 4 or 5 per cent of carbonic acid, sulphuretted hydro-

gen, and olefiant gas The rest is principally carburetted hydrogen, but mixed with some atoms of carbonic oxide and hydrogen The last portion of gas driven off from pit-coal, seems to be entirely carbonic oxide and hydrogen. The distillation of wood and of moist charcoal, and many other vegetable substances, produces carburetted hydrogen, but highly charged with carbonic acid, carbonic oxide and hydrogen , the two last gases always appear exclusively at the end of the process

The properties of carburetted hydrogen are,
1 It is unfit for respiration, and for the support of combustion 2 Its specific gravity when pure, from my experience is very near 6 Dr Henry finds the coal gas to vary from .6 to 78 , but then the heaviest contain 15 per cent of the heavy gases, carbonic acid, sulphuretted hydrogen, and olefiant gas — Water absorbs $\frac{1}{27}$ th of its bulk of this gas — If 100 measures of carburetted hydrogen be mixed with 100 measures of oxygen (the least that can be used with effect), and a spark passed through the mixture, there is an explosion, without any material change of volume after passing a few times through lime water, it is reduced a little, manifesting signs of carbonic acid This residue is found to possess all the characters of a mixture of equal

volumes of carbonic oxide and hydrogen. Upon adding 100 measures of oxygen to this residue and passing a spark, nearly 100 measures of carbonic acid are produced, and the rest of the produce is water. If 100 measures of carburetted hydrogen be put to upwards of 200 of oxygen, and fired over mercury, the result will be a diminution of near 200 measures, and the residuary 100 measures will be found to be carbonic acid.

Though carburetted hydrogen is naturally produced in many coal mines, and occasionally mixing with common air, exhibits some dreadful explosions in the large way, yet when mixed with common air, in Volta's eudiometer, it does not explode by a spark, unless the gas be to the air, as 1 to 10 nearly, and then feebly.

When a portion of carburetted hydrogen gas is electrified for some time, it increases in volume, in the end almost exactly doubling itself, at the same time a quantity of charcoal is deposited. The whole of the gas is then found to be pure hydrogen.

All these facts being compared, there cannot remain the least doubt as to the constitution of carburetted hydrogen. It is a compound of one atom of charcoal and two of hydrogen, the compound atom occupies the same space.

(nearly) as an atom of hydrogen , and 4 atoms of oxygen are necessary to its complete combustion , namely, 2 for the charcoal to form carbonic acid, and 2 for the hydrogen to form water. This conclusion derives a very elegant confirmation, from the facts observed by exploding the gas with one half of the oxygen requisite for complete combustion In this case, each atom of the gas requires only 2 atoms of oxygen , the one joins to one of hydrogen and forms water , the other joins to the carbone to form carbonic oxide, at the same moment the remaining atom of hydrogen springs off Thus there becomes 100 measures of carbonic oxide and 100 of hydrogen, or the same bulk as the original mixture

As the weight of an atom of charcoal is 5 4, and 2 atoms of hydrogen are 2, the compound atom weighs 7 4 , but as there are the same number of atoms of hydrogen and of carburetted hydrogen in the same volume, 7 4 represents the number of times that carburetted hydrogen is heavier than hydrogen Now, the weight of common air is about 12 times as great as hydrogen ; therefore, the relative weights or specific gravities of the two gases, are as 7 4 to 12, or as 6 to 1, nearly, which agrees with experience , hence we derive this conclusion, that carburetted hydrogen consists

entirely of hydrogen and carbone, the whole weight of the gas being accounted for in the carbonic acid and water formed by its combustion *

I think it proper to observe, that, according to my most careful experiments, 100 measures of this gas require rather more than 200 mea-

* According to M Berthollet (*Mém d'Arcueil*, tome 2d) the gas from charcoal is a triple compound of carbone, oxygen, and hydrogen. Whatever our speculative chemists may believe, no practical chemist in Britain adopts this idea. That it always contains more or less of oxygen no one disputes, but then the oxygen is united solely to the carbone forming carbonic oxide. The rest of the mixture consists of carburetted hydrogen and hydrogen. I never find any difficulty in ascertaining the relative quantities of each of the gases in such mixtures. For instance, suppose we take the first of Berthollet's nine specimens

100 gas, sp gr 462 took 81 oxy gave 56 carb acid.

20 carb hyd	sp gr 6	takes 42	— gives 21	—
34 carb ox	—	94	— 16	— 32
46 hyd	—	08	— 23	—
—	—	—	—	—
100 mixt	—	476	takes 81	— gives 53

Here it appears, that 20 measures of carb hyd + 34 carb oxide + 46 hydrogen, constitute a mixture of 100 measures of the sp grav 476, which being burned, take 81 oxygen, and give 53 carb acid. Hence this mixture may be considered as agreeing with Berthollet's gas from charcoal above specified.

450 HYDROGEN WITH SULPHUR

sures of oxygen, and give rather more than 100 carbonic acid, but the difference is not more than 5 per cent and may in general be neglected — Hence, then, we may conclude that the diameter of an atom of carburetted hydrogen is nearly equal to that of hydrogen, but rather less

SECTION 8**HYDROGEN WITH SULPHUR**

There are two compounds of hydrogen with sulphur, the one, a well known elastic fluid denominated *sulphuretted hydrogen*, the other a viscid, oily compound, called *super sulphuretted hydrogen*. The former of these consists of 1 atom of each element,* the latter probably of 1 atom of hydrogen united to 2 of sulphur.

1 *Sulphuretted Hydrogen*

The best way I have found to obtain sulphuretted hydrogen in a pure state, is to heat a piece of iron to a white or welding heat in a

* The figure for sulphuretted hydrogen, plate 4, part 1, is incorrect it ought to be 1 atom of hydrogen instead of 8, united to 1 of sulphur

smith's forge, then suddenly drawing it from the fire, apply a roll of sulphur, the two being rubbed together, unite and run down in a liquid form, which soon fixes and becomes brittle This compound or sulphuret of iron, is to be granulated and put into a gas bottle, to which dilute sulphuric acid is to be added, after which the gas comes over plentifully When the sulphuret of iron is made in a crucible from iron filings and sulphur, it seldom answers well, it often gives hydrogen mixed with the sulphuretted hydrogen The reason seems to be, that several sulphurets of iron exist, namely, the first, the second, the third, &c and it is the second only, or that which is constituted of 1 atom of iron and 2 of sulphur, formed in the process above described, which is essential to the formation of sulphuretted hydrogen The others either give hydrogen or no gas at all

Sulphuretted hydrogen is unfit for respiration and for supporting combustion it has a disagreeable smell, resembling that of rotten eggs, its specific gravity is 1 10 according to Kirwan, and 1 23 according to Thenard Mr Davy, I understand, makes it about 1 13 Some trials of mine a few years since, gave a result near Thenard's, but till a more correct one can be obtained, we may adopt the mean 1 16 Wa-

ter absorbs just its bulk of this gas, whence, therefore, it is mixed with hydrogen, this last will be left after washing in water, or what is still better, in lime water Sulphuretted hydrogen burns with a blue flame. When mixed with oxygen, in the ratio of 100 measures to 50 of oxygen (which is the least effective quantity), it explodes by an electric spark, water is produced, sulphur is deposited, and the gases disappear If 150 or more measures of oxygen are used, then after the explosion over mercury, about 87 measures of sulphurous acid are found in the tube, and 150 of oxygen disappear, or enter into combination with both the elements of the gas

From the experiments of Austin, Henry, &c it has been established, that sulphuretted hydrogen undergoes no change of volume by electrification, but deposits sulphur I have repeated these experiments, and have not been able to ascertain whether there was increase or diminution The residue of gas is pure hydrogen

From these facts, the constitution of sulphuretted hydrogen is clearly pointed out It is 1 atom of sulphur and 1 of hydrogen, united in the same volume as 1 of pure hydrogen When burned, 2 atoms of oxygen unite to 1 of sulphur to form sulphurous acid, and 1 of

oxygen to 1 of hydrogen to form water. The weights of the elements confirm this constitution. One atom of sulphur has been found to weigh 13 (see page 393), to which adding 1 for hydrogen, we obtain the weight of an atom of sulphuretted hydrogen = 14, this number likewise expresses the number of times that sulphuretted hydrogen should exceed hydrogen in specific gravity. But common air exceeds hydrogen 12 times, therefore, 12 : 14 = specific gravity of common air : sp. gravity of sulphuretted hydrogen = 1 : 16, agreeably to the preceding determination. Hence this gas is wholly composed of sulphur and hydrogen, as above.

Sulphuretted hydrogen unites, like the acids, to alkalies, earths, and metallic oxides, forming with them salts of definite proportions, which are called *hydrosulphurates*. Some of these are important chemical agents, but they are apt to undergo changes by keeping, especially in solution.

2 Supersulphuretted Hydrogen

This compound may be obtained as follows. Let half an ounce of flower of sulphur and as much hydrate of lime, be gently boiled together in a quart of rain water for one hour.

more water may be added as it evaporates After cooling, a clear yellow liquid is obtained, which is a solution of sulphuret of lime it will vary in specific gravity from 1 01 to 1 02, according to circumstances — To 6 ounces of this liquid put half an ounce of muriatic acid, and stir the mixture In a short time, the mixture exhibits a milky appearance, and this becomes interspersed with brown oily dots, which gradually subside into an adhesive mass of a semiliquid form at the bottom The liquid may then be poured off, and the brown mass washed with water, which is to be poured off From 20 to 40 grains of this brown oily substance will be obtained, it is supersulphuretted hydrogen.

Scheele, Berthollet, and Proust, have made observations on this compound When exposed to the air, or even in water, it exhales sulphuretted hydrogen, especially if warm On account of its viscosity and adhesiveness, it is very difficult to subject it to experience If a portion of it touch the skin, &c it requires a knife to scrape it off It may be poured from one vessel to another by means of water, which prevents its adhering to the vessel When a little of it is applied to the tongue, a sensation of great heat, and a bitter taste are felt, the saliva becomes white like milk

When liquid alkali is poured upon supersulphuretted hydrogen, heat is produced, hydro-sulphuret is formed, and sulphur precipitated.—These facts have all been observed by me, though few if any of them are new

There is no doubt this substance is formed of sulphur and hydrogen I took 30 grains, and exposed them to a moderate heat in a glass capsule, over a candle, till they ceased to exhale sulphuretted hydrogen The residuum weighed 21 grains, it was soft like clay, when ignited, it burned away with a blue flame, and left no sensible residuum When it is considered, that supersulphuretted hydrogen is from the moment of its formation exhaling sulphuretted hydrogen, we cannot wonder that a portion of it should give less than half its weight of this gas But scarcely any doubt can be raised that the sulphur of the gas is originally equal to that left behind, or that supersulphuretted hydrogen is constituted of 2 atoms of sulphur and 1 of hydrogen, and consequently weighs 27 times as much as hydrogen

Though it is not our present business to explain the previous process by which the article under discussion is obtained, yet, as it will be some time before it comes regularly in our way, it may perhaps be allowable Hydrate

of lime, is 1 atom of lime and 1 of water united, when boiled with sulphur as above, it takes 3 atoms of sulphur. The compound is *sulphuret of hydrate of lime*. When muriatic acid is mixed with it, the acid seizes the lime. The 3 atoms of sulphur divide the atom of water in such sort, that two of them take the hydrogen to form *supersulphuretted hydrogen*, and one takes the oxygen to form *sulphurous oxide*. This last occasions the milkiness of the liquid, by long digestion the milkiness vanishes the sulphurous oxide is changed into sulphuric acid and sulphur, which last falls down, and forms nearly one fourth of that which originally existed in the sulphuret.

SECTION 9.

HYDROGEN WITH PHOSPHORUS

There is only one combination of hydrogen with phosphorus yet known, it is a gas denominated *phosphuretted hydrogen*. This gas may be procured as follows. Let an ounce or two of hydrate of lime (dry slacked lime) be put into a gas bottle or retort, and then a few small pieces of phosphorus, amounting to 40 or 50 grains. If the materials are sufficient to

fill the bottle, no precaution need be used; but if not, the bottle or retort should be previously filled with azotic gas, or some gas not containing oxygen, in order to prevent an explosion. The heat of a lamp is then to be applied, and a gas comes which may be received over water. This gas is phosphuretted hydrogen, but sometimes mixed with hydrogen. Liquid caustic potash may be used instead of hydrate of lime, in order to prevent the generation of hydrogen.

Phosphuretted hydrogen gas has the following properties. 1 When bubbles of it come into the atmosphere, they instantly take fire, an explosion is produced, and a ring of white smoke ascends, which is phosphoric acid. 2 It is unfit for respiration, and for supporting combustion. 3 Its specific gravity is 85, common air being denoted by unity. 4 Water absorbs $\frac{1}{7}$ th of its bulk of this gas. 5 If the gas be electrified, the phosphorus is thrown down, and there finally remains the bulk of the gas of pure hydrogen. In fact, the phosphorus is easily thrown down, either by electricity, by heat, or by being exposed to a large surface of water. In this respect, phosphuretted hydrogen is nearly related to sulphuretted hydrogen.

Though phosphuretted hydrogen explodes

when sent into the atmosphere in bubbles, yet if sent into a tube of three tenths of an inch diameter, it may be mixed with pure oxygen, without any explosion. In all the experiments I have made, which are more than 20, I never had an instance of a spontaneous explosion. In this case, an electric spark produces a most vivid light, with an explosion not very violent, phosphoric or phosphorous acid and water are produced

My experiments on the combustion of this gas give the following results. When 100 measures of pure phosphuretted hydrogen are mixed with 150 of oxygen, and exploded, the whole of both gases disappears, water and phosphoric acid are formed, when 100 measures of the gas are mixed with 100 oxygen, and fired, the whole of both gases still disappears, in this case, water and phosphorous acid are formed, when 100 measures are mixed with less than 100 of oxygen, phosphorous acid and water are formed, but part of the combustible gas remains unburnt

As this gas is liable to be contaminated with hydrogen, sometimes largely, on account of the facility it possesses of depositing phosphorus, it is expedient to ascertain the exact proportion of phosphuretted hydrogen to hydrogen in any proposed mixture. This I find

may easily be done Whenever a sufficient quantity of oxygen is afforded, the whole of the combustible gas is consumed The exact volume of oxygen and its purity must be noted , the quantity of oxygen in the residue must also be noted Then the total diminution after the explosion, being diminished by the oxygen consumed, leaves the combustible gas Now, as phosphuretted hydrogen takes $1\frac{1}{2}$ times its bulk of oxygen, and hydrogen takes $\frac{1}{2}$ its bulk of oxygen , we shall obtain the following equations, if P denote the volume of phosphuretted hydrogen, H that of hydrogen, O that of oxygen, and S = P + H, the whole of the combustible gas

$$\begin{aligned}P &= O - \frac{1}{2}S \\H &= 1\frac{1}{2}S - O\end{aligned}$$

From these equations, the ratio of the two gases in any mixture is deduced The analysis may be corroborated as follows To any mixture containing a certain volume of phosphuretted hydrogen, let the same volume of oxygen be added , after the explosion, the diminution will be just twice the volume of oxygen In this case, the phosphuretted hydrogen is preferred by the oxygen , phosphorous acid and water are formed, and the hydrogen remains in the tube If more ox-

gen is put than the phosphuretted hydrogen, then the diminution after firing is more than twice the oxygen

The investigation respecting the proportion of hydrogen mixed with phosphuretted hydrogen, was instituted chiefly in consequence of a difference of opinion respecting the specific gravity of the latter gas I had found 100 cubic inches to weigh about 26 grains, Mr. Davy informed me he had found 100 inches to weigh only 10 grains the difference is enormous I requested Dr Henry would assist me in repeating the experiment We obtained a gas, such that 100 inches weighed 14 grains, this result surprized me, but upon burning the gas with oxygen, it was found only to take its bulk of that gas, and consequently to be half hydrogen and half phosphuretted hydrogen, which satisfactorily explained the difficulty Mr Davy's gas, I conceive, must have been $\frac{1}{3}$ phosphuretted hydrogen and $\frac{2}{3}$ hydrogen, at the time it was weighed, however this may be, it is evident, from what is related above, that nothing certain can be inferred relative to the specific gravity of this gas, unless a portion of the gas be analyzed previously to its being ' $\frac{1}{3}$ ' I, a circumstance of which I was not at first sufficiently aware

I have recently procured some phosphuretted hydrogen gas from caustic potash and phosphorus, an accident prevented me obtaining a sufficient quantity to weigh, but I got 5 or 6 cubic inches, which of course were mixed with the azotic gas previously put into the retort. The pure combustible gas was of such character, that 100 measures required only 85 of oxygen for their combustion, it was consequently 35 phosphuretted hydrogen and 65 hydrogen per cent and probably would have weighed after the rate of 10 or 11 grains for 100 cubic inches. I expected much purer gas.

As to the constitution of phosphuretted hydrogen, it is clearly 1 atom of phosphorus united to 1 of hydrogen, occupying the same space as 1 of elastic hydrogen. In combustion, the atom of hydrogen requires one of oxygen, and the atom of phosphorus requires one or two of oxygen, according as we intend to produce phosphorous or phosphoric acid. Hence it is that 100 measures of phosphuretted hydrogen require 50 oxygen to burn the hydrogen, 50 more of oxygen to form phosphorous acid, and 50 more to form phosphoric acid. The weight of the gas corroborates this conclusion. It has been seen that the atom of phosphorus weighs nearly 9 (page 415), this

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would make the specific gravity of phosphuretted hydrogen equal to 10 times that of hydrogen, which it actually is, or nearly so, from the foregoing experiments

The next compounds to be considered in course, would be those of *azote* with *carbone*, with *sulphur*, and with *phosphorus*, but such compounds either cannot be formed, or they are yet unknown

SECTION 10

CARBONE WITH SULPHUR, WITH PHOSPHORUS, AND SULPHUR WITH PHOSPHORUS

1 *Carbone with Sulphur*

In the 42d vol of the *An de Chimie*, page 136, Clement and Desormes have announced a combination of carbone and sulphur, which they call *carburetted sulphur*. They obtain it by sending the vapour of sulphur over red hot charcoal, it is collected in water in the form of an oily liquid of the specific gravity 1 3. This liquid is volatile, like ether, expanding any gas into which it is admitted, and forming

a permanent elastic fluid over the mercury of a barometer No gas is produced at the same time as the liquid When too much sulphur is driven through, instead of a liquid, a solid compound is formed which crystallizes in the tube They seem to have shewn that the compound does not contain sulphuretted hydrogen.—In the 64th vol of the Journal de Physique, A B Berthollet endeavours to prove that the liquid in question is a compound of hydrogen and sulphur, and contains no charcoal The facts adduced are not sufficient to decide the question either way I should be unwilling to admit, with Clement and Desormes, that the two inelastic elements, charcoal and sulphur, would form an elastic or volatile compound , yet, they have rendered it highly probable that charcoal makes a part of the compound, as it disappears during the process I think it most probable, that Berthollet is correct in the idea that this liquid contains hydrogen We know of no other volatile liquid that does not contain hydrogen Perhaps it will be found a triple compound of hydrogen, sulphur, and charcoal

2 Carbone with Phosphorus

A combination of carbone and phosphorus has been pointed out by Proust, in the 49th volume of the Journal de Physique, which he names *phosphuret of carbone*. It is the reddish substance which remains when new made phosphorus is strained through leather in warm water. The proportion of the two elements has not been ascertained.

3 Sulphur with Phosphorus

Melted phosphorus dissolves and combines with sulphur, and that in various proportions, which have not yet been accurately ascertained. The compounds may be denominated *sulphurets of phosphorus*. The method of forming these compounds, is to melt a given weight of phosphorus in a tube nearly filled with water, and then to add small pieces of sulphur, keeping the tube in hot water, taking care not to exceed 160°, or 170°, or 180°, because the new compound begins to decompose water rapidly at those high temperatures. Pelletier has given us some facts towards a theory of these various combinations, in the

4th vol of the *Ann de Chimie* He found that a mixture of sulphur and phosphorus remained fluid at a much lower temperature than either of them individually , and that different proportions gave different fusing or congealing points One part of phosphorus, combined with $\frac{1}{8}$ th of sulphur, congealed at 77° , one part with $\frac{1}{4}$, at 59° , one part with $\frac{1}{2}$, at 50° , one part with 1, at 41° , one part with 2, at $54^{\circ}\frac{1}{2}$, but a certain portion was fluid, and the rest solid , and one part with 3, at $99^{\circ} 5$

One would be apt to think, from these experiments, that sulphur and phosphorus might be combined in all proportions , but the observation on the 5th led me to suspect that it might have been applied to some others if the results had been carefully noted —I mixed $18\frac{1}{2}$ grains of phosphorus and 13 of sulphur in a graduated tube, put in water, and immersed the whole into water of 160° The phosphorus having been rendered fluid as usual, at 100° , gradually reduced the sulphur, till the whole assumed a liquid form of the specific gravity 1 14 It remained uniformly fluid at 45° , but was wholly congealed at 42° Here were two atoms of phosphorus united to one of sulphur I then added $6\frac{1}{2}$ grains of sulphur, making the mixture $18\frac{1}{2}$ phosphorus, and $19\frac{1}{2}$

sulphur, this new mixture was reduced to uniform fluidity at 170° , and was of 1 47 specific gravity, reduced to 47°, one part was fluid and the other solid, the latter being at the bottom of the tube This solid part was not completely reduced to fluidity in the temperature 100° This seems to indicate that two distinct combinations took place , the one, two atoms of phosphorus and one of sulphur, liquid at 47° , the other, one atom of phosphorus and one of sulphur, solid under 100° I next added $6\frac{1}{2}$ grains more of sulphur, making in the whole $18\frac{1}{2}$ phosphorus and 26 sulphur, consequently in such proportion as to afford a union of one atom of each , the union was completed in a temperature of 180° the specific gravity was 1 50 Cooled down to 80° , the whole was solid , heated to 100° , the whole became a semi-liquid, uniform mass Being afterwards heated to 140° , the whole became fluid , but upon cooling again, the greatest part congealed at 100° , but $\frac{1}{3}$ d or $\frac{1}{4}$ th remained liquid down to 47° —From these experiments, it is most probable that one atom of each forms a combination which is solid at 100° or below , but that being heated, it is apt to run into the other mode of combination, or that constituted of two atoms of phosphorus and one of sulphur The properties of these

two species of sulphuret of phosphorus I have not had an opportunity to investigate. The water in the tube is evidently decomposed in part by the compound, it becomes milky, probably through the oxide of sulphur, and both sulphuretted and phosphuretted hydrogen seem to be formed in small quantities at temperatures above 160°.

SECTION II

FIXED ALKALIES

The fate of the two fixed alkalies, potash and soda, has been rather remarkable. They had long been suspected to be compound elements, but no satisfactory proof was given. At length Mr Davy, by his great skill and address in the application of galvanism to produce chemical changes, seemed to have established the compound nature of these elements, both by analysis and synthesis. They appeared to be *metallic oxides*, or peculiar metals united to oxygen. Consistent with this idea, some account of the metals, denominated *potassium* and *sodium*, has been given in this work. (See page 260) But from what follows, it appears most probable, that these metals are

compounds of potash and soda with hydrogen, and that the two fixed alkalies still remain among the undecomposed bodies

1 *Potash*

Potash is obtained from the ashes of burned wood Water dissolves the saline matter of the ashes, and may then be poured off and evaporated by artificial heat the salt called *potash* remains in the vessel If the salt so obtained be exposed to a red heat, it loses combustible matter, becomes white, and is in part purified in commerce it is then called *pearl-ash* This mass is still a mixture of various salts, but is constituted chiefly of *carbonate of potash* In order to obtain the potash separate, let a quantity of *pearl-ash* (or what is still better, *salt of tartar* of the shops, which is this pearl-ash reduced almost to pure carbonate of potash) be mixed with its weight of water, and the mixture be stirred , after the undissolved salt has subsided, pour off the clear solution into an iron pan, and mix with it a portion of hydrate of lime, half the weight of the liquid , then add a quantity of water equal to the weight of the ingredients, and boil the mixture for several hours, occasionally adding more water to supply the waste When

the liquid is found not to effervesce with acids, the ebullition may be discontinued After the lime has subsided, the clear liquid is to be decanted, and then boiled down in a clean iron pan till it assumes a viscid form, and acquires almost a red heat It may then be poured into molds, &c and it immediately congeals The substance so obtained is potash nearly pure, but it still contains a considerable portion of water, some foreign salts, oxide of iron, and frequently some unexpelled carbonic acid The water may amount to 20 or 25 per cent upon the whole weight, and the other substances to 5 or 10 per cent In this process, the carbonic acid of the potash is transferred to the lime

If potash of still greater purity be required, the method practised by Berthollet may be pursued The solid potash obtained as above must be dissolved in alcohol, the foreign salts will fall to the bottom insoluble, the liquid solution may then be decanted into a silver basin, the alcohol be evaporated, and the fluid potash exposed to a red heat It may be poured out upon a clean polished surface, where it instantly congeals into solid plates of potash, which are to be broken and put into well stoppered bottles, to prevent the access of air and moisture This potash is a solid,

brittle, white mass, consisting of about 84 parts potash and 16 water, in 100 parts, and is the purest that has ever yet been obtained.

Potash may be exhibited in a more regular crystalline form by admitting more water to it. If the solution be reduced to the specific gravity of 1 6, or 1 5, upon cooling, crystals will be formed, containing about 53 per cent. of water, or more, if the air is cold. These crystals are called *hydrate of potash*. Hence solid hydrate of potash may be formed, containing from 84 per cent of potash to 47, or under

Potash has a very acrid taste, it is exceedingly corrosive if applied to the skin, so as to obtain the name of *caustic*. The specific gravity of the common sticks of potash used by surgeons, I find to be 2 1, but these are a mixture of potash and carbonate of potash, with 20 or 30 per cent of water. If pot-ash were obtained pure, I apprehend its specific gravity would be about 2 1

When crystals of potash (that is the hydrate) are exposed to heat, they become liquid, the water is gradually dissipated with a hissing noise, till at length the fluid acquires a red heat. It then remains tranquil for some time, but if the heat be increased, white fumes begin to arise copiously. The alkali and water

both evaporate in this case, therefore, the process cannot be used to expel the last portion of water from the alkali. If the hydrate be taken in the red hot and tranquil state, it contains 84 per cent potash and 16 water. This is ascertained by saturating a given weight of it with sulphuric acid, when sulphate of potash is formed free from water, and 100 parts of the hydrate give only 84 parts to the new compound.

Water has a strong affinity for potash. If a portion of the 84 per cent hydrate be put into as much water, great heat is immediately produced, equal to that of boiling water. But it is observable that the crystallized hydrate containing much water, when mixed with snow, produces excessive cold. When potash is exposed to the air, it attracts moisture and carbonic acid, becoming a liquid carbonate. Potash dissolved in water, and kept in a stoppered bottle, retains its causticity. It is called *alkaline ley*, and may be had of various strengths and specific gravities.

Potash, and the other alkalies, change vegetable colours, particularly blues, into green.—Potash is of great utility in the arts and manufactures, particularly in bleaching, dyeing, printing, soap and glass manufactures. It unites with most acids to form salts. It does

not unite with any of the simple substances, as far as is yet known, except hydrogen, and that in a circuitous way, as will presently be noticed. The hydrate of potash unites with sulphur, but the compound, consisting of three or more principles, cannot yet be discussed.

The theory of the nature and origin of potash still remains in great obscurity. The great question, whether it is a constituent principle of vegetables, or formed during their combustion, is not yet satisfactorily answered. One circumstance is favourable to the investigation of the nature of potash, the weight of its ultimate particle is easily ascertained, it forms very definite compounds with most of the acids, from which it appears to be 42 times the weight of hydrogen. The following proportions of the most common salts with base of potash, are deduced from my experience; they are such that good authorities may be found both for greater and less proportions of the different elements.

per cent.

Carbonate of potash, 31 1, acid + 68 9 base, as 10	42
Sulphate ——— 44 7 — + 55 3 —	34 42
Nitrate ——— 47 5 — + 52 5 —	38 42
Muriate ——— 31 1 — + 69 6 —	22 42

The above salts are capable of sustaining a red heat, and may therefore be supposed to be free from water, at all events, the potash must contain the same quantity of water in combination with the respective acids, as appears from the uniformity of its weight. The above numbers, 19, 34, 38 and 22 represent, as the reader will recollect, the weights of the atoms of the respective acids, except the nitric, which is double. As water has so strong an affinity for potash, and as the weight of the elementary particle of potash above deduced is more than five times that of water, it may still be supposed that water enters into the constitution of potash, or that it is compounded of some of the lighter earths with azote, oxygen, &c. From present appearances, however, the notion that potash is a simple substance seems more probable than ever.

From the above observations, it appears that potash ought still to be considered as a simple substance, and would require to be placed among such substances, but that it cannot be obtained alone. In that state which approaches nearest to purity it is a hydrate, containing at least 1 atom of water united to 1 of potash, amounting to 16 per cent of water. This hydrate is therefore a *ternary compound*, or one of three elements, and ought to be post-

poned till the next chapter but, in the present state of chemical science, utility must be allowed in some instances to supersede methodical arrangements The fixed alkalies are most useful chemical agents, and the sooner we become acquainted with them the better, more especially, as some of the first chemists of the present age have been led into considerable mistakes, by presuming too much upon their knowledge of the nature and properties of these familiar articles

In the *Mémoires de l'Institut de France*, 1806, Berthollet published researches on the laws of affinity, from which some extracts are given in the *Journal de Physique* for March 1807 — By these, it appears that he found sulphate of barytes to consist of 26 acid and 74 base, and sulphate of potash of 33 acid and 67 base The former of these results was corroborated by the previous experience of Thenard, but both are so remote from the uniform results of other chemists, that they could never be generally adopted At length Berthollet discovered the error, and has announced it in the 2d vol of the *Mémoires d'Arcueil* It consisted in mistaking the hydrates of barytes and potash for pure barytes and potash It seems to have been generally adopted, but certainly prematurely, that barytes and potash,

in a state of fusion, were pure, or free from water. But upon due investigation, he found that fused potash contains 14 per cent of water. my experience as well as theory, leads me to adopt 16 per cent of water, which accords with the position of 1 atom of each of the elements uniting to form the hydrate; namely, 42 by weight of potash with 8 of water. This discovery reconciles the jarring results on the proportions of the above neutral salts, and throws light upon some other interesting subjects of chemical analysis.

2 *Hydrate of Potash*

Upon turning my attention to this subject, I soon perceived the want of a table exhibiting the relative quantities of potash and water in all the combinations of these two elements. In a state of solution, the specific gravity may be taken as a guide, but this is not quite so convenient when the compound is in a solid form. I found nothing of the kind in any publication, and therefore undertook a course of experiments to determine the relative quantities of potash, &c in the various solutions. The results are contained in the following table, which I would have to be considered

only as an approximation to truth, but it will certainly have its use till a more complete and accurate one be obtained Dr Henry was so obliging as to facilitate my progress, by presenting me with portions of the fixed alkalies, prepared after Berthollet's method.

Table of the quantity of real potash in watery solutions
of different specific gravities, &c.

Atoms. Potash Water	Potash per cent. by weight	Pota h per cent. by measure	Specific gravity	Congealing point	Boiling point
1+ 0	100	240	2 4	unknown	unknown
1+ 1	84	185	2 2	1000°	red heat
1+ 2	72 4	145	2 0	500°	600°
1+ 3	63 6	119	1 88	340°	420°
1+ 4	56 8	101	1 78	220°	360°
1+ 5	51 2	86	1 68	150°	320°
1+ 6	46 7	75	1 60	100°	290°
1+ 7	42 9	65	1 52	70°	276°
1+ 8	39 6	58	1 47	50°	265°
1+ 9	36 8	53	1 44	40°	255°
1+ 10	34 4	49	1 42		246°
	32 4	45	1 39		240°
	29 4	40	1 36		234°
	26 3	35	1 33		229°
	23 4	30	1 28		221°
	19 5	25	1 23		220°
	16 2	20	1 19		218°
	13	15	1 15		215°
	9 5	10	1 11		214°
	4 7	5	1 06		213°

Remarks on the Table

The first column contains the number of atoms of potash and water in the several com-

bination to 10 atoms of water · the weight of an atom of potash is taken to be 42, and 1 of water 8 From these data the second column is calculated There did not appear any striking characteristic of distinction between the first, second, third, &c. hydrates, (if they may be so called) except that the first bears a red heat in the liquid form, with tranquillity and without loss of weight Before this, the water is gradually dissipated with a hissing noise and fumes I remarked, however, that when a solution of potash is boiled down till the thermometer indicates upwards of 300° , the evaporation of the water, and the rise of the thermometer, are desultory , that is, the operations appear somewhat stationary for a time, and then advance quickly , how far this may arise from the nature of the compound, or from the imperfect conducting power of the liquid in those high temperatures, I could not determine without more frequent repetitions of the experiment

The third column is, as usual, obtained by multiplying the second column by the specific gravity , it is often more convenient in practice to estimate quantity by measure than by weight

The fourth column denotes the specific gravity , below 1 60 the hydrate is completely

fluid, or may be made so by a moderate heat, but above that temperature, I found some difficulty in ascertaining the specific gravity, and was obliged sometimes to infer it from the tenor of the table. The common sticks of potash of the druggists are of the sp gr 21, which I found by plunging them into a graduated tube filled with mercury, and marking the quantity that overflowed. These sticks are a mixture of hydrate and carbonate. Real potash must, I conceive, be heavier than they are. The relation of the second and fourth columns was ascertained by taking a given weight of the alkaline solution, saturating it with test sulphuric acid (1134), and allowing 21 grains of alkali for every 100 measures of acid (containing 17 real) which the alkali required.

The 5th column denotes the temperatures at which the different hydrates congeal or crystallize. This part of the subject deserves much more accurate enquiry than I have been able to bestow upon it. No doubt the different hydrates might be distinguished this way. Proust talks of a crystallized hydrate of potash, containing 30 per cent of water, and Lowitz of one containing 43 per cent. of water. They calculate, I presume, upon the supposition of fused potash being free from water, if so,

Proust's hydrate is the fourth of our table, and Lowitz's the sixth I would not have much trust to be put in the temperatures I have marked in this column

The sixth column indicates the temperatures at which the different specific gravities boil This is easily ascertained, except for the high degrees, in which an analysis of the hydrate was required upon every experiment I believe the results will be found tolerably accurate As the range of temperature is large, this may be found a very convenient method of ascertaining the strength of alkaline solutions, when the specific gravities are unknown

3 *Carbonate of Potash*

Though it be premature to enter into the nature of carbonate of potash, a triple compound, yet its utility as a test is such as to require it to be noticed in the present section Indeed it may generally be a substitute for the hydrate of potash, and it can much more readily be procured in a state of comparative purity The carbonate I mean is that which consists of one atom of acid united to one of potash, which by some writers is called a *sub-carbonate* It is, of course, constituted of 19

parts of acid by weight united to 42 of potash This salt is to be had in tolerable purity of the druggists, under the name of *salt of tartar*, but when it is to be used in solution for pure carbonate, a large quantity of the salt, and a small quantity of water, are to be mixed and agitated, then let the undissolved salt subside, and pour off the clear solution, which may be diluted with water, &c

This salt is well known to be, like the dry hydrate of potash, very deliquescent I took 43 grains of carbonate of potash that had just before been made red hot, put them into a glass capsule exposed to the air, in one day the weight became 50 grains, in three days, 61 grains, in seven days, 75 grains, in 11 days, 89 grains, in 21 days, 89+ grains, in 25 days, 90 grains The specific gravity was 1 5 + nearly All the water is, however, driven off by a moderate heat, namely, that of 280° It supports a high red heat before fusion, and when fused loses no weight, remaining without sublimation, and undecomposed I ascertained that it was a perfect carbonate, by dissolving 61 grains of pure dry salt in lime water, when 12 grains of carbonate of lime were thrown down, corresponding to 19 grains of carbonic acid

Table of the quantity of real carbonate of potash in watery
solutions of different specific gravities.

Atoms. Carb of Pot Water	Carb Potash per cent by weight	Carb Potash per cent by measure	Specific gravity	Boiling point.
1+ 0	100	260	2 60	280°
1+ 1	88 4	212	2 40	265°
1+ 2	79 2	170	2 15	258°
1+ 3	71 8	140	1 95	252°
1+ 4	65 6	118	1 80	247°
1+ 5	60 4	103	1 70	244°
1+ 6	56	91	1 63	241°
1+ 7	52 1	82	1 58	238°
1+ 8	48 8	75	1 54	235°
1+ 9	45 8	69	1 50	232°
1+10	43 3	63	1 46	229°
	41 7	60	1 44	227°
	39	55	1 41	225°
	36 2	50	1 38	222°
	33 5	45	1 34	220°
	30 5	40	1 31	218°
	27 3	35	1 28	217°
	24	30	1 25	216°
	20 5	25	1 22	215°
	16 8	20	1 19	214°
	13 2	15	1 15	214°
	9	10	1 11	213°
	4 7	5	1 06	213°

This table is similar in structure to the preceding. The first column contains the number of atoms of water joined to one of carbonate of potash, which last weighs 61. The second contains the weight of carbonate of potash per cent in the compound, and the third the grains of carbonate in 100 water grain measures of the compound, found by multiplying

the numbers in the second and fourth columns together The fourth contains the specific gravities , the relations of these to the quantities in the second column were found, by taking a given weight of the solution, and saturating it with a certain number of measures of test sulphuric acid (1 134), allowing 21 real potash, or $30\frac{1}{2}$ carbonate, for every 100 measures of acid required , because such acid contains 17 per cent by measure of real sulphuric acid, and that requires 21 of potash

The strongest solution of this salt that can be obtained is of the specific gravity 1 54 This consists of 1 atom of carbonate and 8 of water , but by putting dry carbonate into that solution, various mixtures may be formed up to the specific gravity 1 80 , above that the specific gravity is scarcely to be obtained but by inference I could not obtain a solid stick of fused carbonate but what was spongy, I suppose from incipient decomposition It may be observed, that the specific gravity 1 25, which contains 30 per cent of carbonate, is that which I prefer as a test for acids , because the solution contains 21 per cent pure potash, and 100 measures of it consequently require 100 measures of the test acids

I found a specimen of the pearl ash of commerce to contain 54 parts carbonate of potash,

22 parts of other salts, and 24 parts of water in the hundred

The fifth column denotes the temperature at which the saline solutions boil This will be found generally a good approximation to truth. I observed the thermometer did not rise above 280° as long as any visible moisture remained , as soon as that vanished, the salt assumed the character of a hard and perfectly dry substance

In the course of these experiments, I took a quantity of carbonate of potash, and heated it red hot , then weighed it , after which I put to it as much water as afforded 1 atom to 1 , namely, 8 parts water to 61 salt The salt was then pulverized in a mortar , it was put out upon white paper, and appeared a white, dry salt , but upon pouring it back into the mortar, some particles of the salt adhered to the paper The same quantity of water was again put to it Upon mixing them with a knife, the whole mass assumed a pasty consistence, and adhered to the knife in the shape of a ball , after being well rubbed in the mortar, it again assumed a white, dry appearance Upon paper, it seemed like salt of tartar some time exposed to the air Several particles stuck to the paper, but were easily removed by a knife The addition of another

atom of water reduced the compound to the consistence of bird-lime, but after standing it cut like half dried clay. The next atom of water reduced it to the consistence of bookbinders paste. The fifth atom of water reduced it to a thick fluid, consisting of dissolved and undissolved salt. This, by the successive application of like portions of water, became a perfect fluid with 8 atoms of water to 1 of carbonate of potash. Its specific gravity was 1.5, but there was some undissolved sulphate of potash subsided, the salt of tartar not having been previously purified.

4 Potassium, or Hydruret of Potash

Since writing the articles on Potassium and Sodium (page 260 and seq.), and the subsequent articles on fluoric and muriatic acid (page 277 and seq.), a good deal more light has been thrown on these subjects. Two papers on the subjects have been published by Mr Davy, a series of essays by Gay Lussac and Thenard, are contained in the 2d vol of the *Memoires d'Arcueil*, the same volume also contains a paper by Berthollet, announcing an important discovery relating to the fixed alkalies, namely, that in a state of fusion by

heat, they contain a definite proportion of water in chemical combination Upon re-considering the former facts, and comparing them with the more recent ones, I am obliged to adopt new views respecting the nature of these new metals Mr Davy still adheres to his original views, and which indeed were the only rational ones that could be formed (supposing the fused alkalies to contain no water), namely, that potash is the oxide of potassium , Gay Lussac and Thenard, on the contrary, consider potash as undecomposed, and potassium a compound of hydrogen and potash, analogous to the other known compounds of hydrogen and elementary principles This last is the only one, I think, that can be admitted either from synthetic or analytic experiments, so as to be reconcileable with the facts , but I do not coincide with all the conclusions which the French chemists have deduced Mr Davy has furnished us with the most definite and precise facts , and though I was led to controvert some of them (see page 289 and seq), it was principally through my having adopted his views of the nature of potassium I am now persuaded those results were more accurate than I imagined

Mr Davy first attempted to decompose the fixed alkalies, by applying Voltaic electricity

to saturated watery solutions, in this case, oxygen and hydrogen gas were obtained, evidently proceeding, as he concluded, from the decomposition of the water. But when any potash that had previously been fused, was substituted for the watery solution, no hydrogen gas was given out at the negative pole, but potassium was formed, and pure oxygen was given out at the positive pole. The residual potash was unaltered. The conclusion he drew was, that the potash was decomposed into potassium and oxygen. But it now appears, that fused potash is composed of 1 atom of water and 1 of potash. The electricity operates upon this last atom of water to separate its elements, it succeeds in detaching the atom of oxygen, but that of hydrogen draws the atom of potash along with it, forming an atom of potassium. The atom of hydrate weighing 50 (= 42 potash + 8 water) is decomposed into one of potassium, weighing 43, and one of oxygen weighing 7. Hence the atom of potassium is composed of 1 potash + 1 hydrogen, weighing 43, and not of 1 potash — 1 oxygen, weighing 35, as stated at page 262.

The method of obtaining potassium, discovered by the French chemists, is to find the first hydrate of potash in a state of vapour over

red hot iron turnings, in an iron tube intensely heated, hydrogen gas is given out, potassium is formed and condensed in a cool part of the tube, and part of the potash is found united to the iron In this mode of producing potassium, its constitution is not so obvious as in the former The two methods, however, together, shew that fused potash contains both oxygen and hydrogen, which is now abundantly confirmed by experiments of a different kind It seems probable that in the latter method the hydrate of potash is partly decomposed into potash and water, and partly into potassium and oxygen , in both cases the iron acquires the oxygen

The specific gravity of potassium is 6, or 796, according to Davy , but 874 according to Gay Lussac and Thenard The levity of it, combined with its volatility at a low red heat, agrees with the notion of its being potash and hydrogen, or *potasseted hydrogen*, resembling the other known compounds of sulphur, phosphorus, charcoal, arsenic, &c combined with hydrogen

When burned in oxygen gas, potassium produces potash as dry as possible to be procured, according to Mr Davy , that is, the first hydrate When potassium is thrown into water it burns rapidly, decomposing the water, and

giving off hydrogen Calculating the oxygen from the quantity of hydrogen, Mr Davy finds 100 (hydrate of) potash contain from 13 to 17 oxygen Gay Lussac seems to make it 14 For, 2284 grammes of potassium gave 649 cubic centimetres of hydrogen, reduced, 355 grains gave 345 cubic inches English measure, which correspond to 1725 inches of oxygen = 59 grains Hence $353 + 59 = 412$ grains of hydrate, and $412 - 59 = 100 - 14$. But this is exactly the quantity that theory would assign, for, 43 potassium + 7 oxygen = 50 hydrate, which gives just 14 oxygen in the hundred

Potassium burns spontaneously in oxymuriatic acid gas, muriate of potash is formed, and probably water It decomposes sulphuretted, phosphuretted, and arseniuretted hydrogen gas, accord^g to Gay Lussac and Thenard, and unites to the sulphur, &c with some of the hydrogen Mr Davy finds tellurium to unite with the hydrate of potash by Voltarc electricity without decomposing it Potassium burns in nitrous gas and nitrous oxide, forming dry hydrate of potash, and evolving azote It burns in sulphurous and carbonic acid, and in carbonic oxide, hydrate of potash which unites to the sulphur is formed, or hydrate of potash and charcoal

The combustion of potassium in muriatic acid gas is particularly worthy of notice Both Mr Davy and the French chemists agree that when potassium is burned in muriatic acid gas, muriate of potash is formed, and hydrogen evolved, which agrees in quantity with that evolved in the decomposition of water by the same quantity of metal But, what is most astonishing, they both adopt the same explanation, when their different views of the constitution of potassium require them to be opposite Mr Davy had two ways in which he might account for the phenomenon, the one was to suppose that a part of the acid was decomposed, and furnished the oxygen to the metal to form the oxide (potash), which joined to the remainder of the acid, and the hydrogen was an evolved elementary principle of that part of the acid decomposed , and the other, to suppose that the acid gas contained in a state of union just as much water as was sufficient to oxidate the metal (this would have been thought an extraordinary circumstance a few years ago) Either of these positions was consistent , but he adopted the latter, and seemed to confirm it by shewing that a given quantity of muriatic acid gas afforded the same quantity of muriate of silver, whether combined previously with potash or potassium

This explanation did not meet my views as well as the former I endeavoured to account for the facts (page 289) on the notion of a decomposition of the acid Two circumstances conspired to incline me to this view The one was, that hydrogen seemed on other accounts to be a constituent of muriatic acid , the other was, that water does not appear in any other instance to be combined with any elastic fluid , I mean in such way that if the water be removed, the rest of the molecule will carry along with it the character of the whole In one respect I mistook the data, having over-rated the weight of muriatic acid gas —I would now be understood to abandon the explanation founded on the decomposition of the acid , and to adopt the much more simple one that the muriatic acid combines with the potash of the potassium, at the same instant expelling the hydrogen , in this way there is no occasion for any water either combined or otherwise It exceeds my comprehension how Gay Lussac and Thenard should insist so largely on the opinion that muriatic acid gas contains water, and that principally, as it should seem, in order to account for the hydrogen evolved during the combustion of potassium, and the supposed oxydation of the metal

It has been stated that potassium burns in silicated fluoric acid gas (page 283), the result is fluate of potash and some hydrogen. The theory of this is not obvious

Potassium acts upon ammoniacal gas Mr Davy found that when 8 grains of the metal were fused in ammoniacal gas, between $12\frac{1}{2}$ and 16 cubic inches of the gas were absorbed, and hydrogen evolved corresponding to the oxydation of the metal by water, that is, 1 atom of hydrogen for 1 atom of potassium. The new compound becomes of a dark olive colour By applying a greater degree of heat the ammonia is in part expelled again, but part is also decomposed Gay Lussac and Thenard say, that by admitting a few drops of water to the compound, the whole of the elements of the ammonia are recoverable, and nothing but caustic potash remains Mr Davy affirms the results of the decomposition to be somewhat different It seems pretty evident, that in this process two atoms of ammonia unite to one of potassium, expelling its hydrogen at the same moment For, 43 grains of potassium would require 12 of ammonia, and therefore 8 will require $2\frac{1}{4}$ grains, which correspond to $12\frac{1}{2}$ cubic inches

5 Soda

Soda is commonly obtained from the ashes of plants growing on the sea-shore, particularly from a genus called *salsola*, in Spain, where this article is largely prepared, it is called *barrilla*. In Britain, the various species of *fucus* or sea-weed are burnt, and their ashes form a mixture containing some carbonate of soda, this mixture is called *kelp*. Soda is found in some parts of the earth combined with carbonic acid, and in others combined with muriatic acid, as minerals, and hence it has been called the *fossil* or *mineral* alkali, to distinguish it from potash or the *vegetable* alkali.

To obtain soda in as pure a state as possible, recourse must be had to a process similar to that for obtaining potash. Pure carbonate of soda must be treated with hydrate of lime and water, the carbonate of soda is decomposed, the soda remains in solution in the liquid, the carbonic acid unites to the lime and the new compound is precipitated. Afterwards the clear liquid must be decanted and boiled down, the water gradually goes off with a hissing noise till the soda acquires a low red heat, when the alkali and remaining water become a tranquil liquid. This liquid may be

run out into molds, &c when it instantly congeals into a hard mass, and is then to be preserved in bottles for use If still greater heat be applied, the alkali and water are together dissipated in white fumes

Soda thus obtained is a solid, brittle, white mass, consisting of about 78 parts pure soda and 22 water per cent , according to d'Arcet (*Annales de Chimie*, Tome 68, p 182) the alkali is only 72 , but I believe that is too low With more water, soda may be had in crystals, like potash, probably containing 50 or 60 per cent of water Soda, like potash, is extremely caustic , it is deliquescent, and produces heat when dissolved in water The specific gravity of fused soda I find to be 2, by pouring it into a graduated glass tube There is some reason to apprehend that pure soda, could it be obtained, would be specifically heavier than potash, though its ultimate particle is certainly of less weight than that of the latter The properties and uses of soda are much the same as those of potash , indeed, the two alkalies were long confounded, on account of their resemblance The compounds into which they enter are in many instances essentially different, and the weights of their atoms are very unequal The origin of soda in vegetables is somewhat obscure, though it may be derived

from the muriate of soda in the water of the sea

The weight of an atom of soda is easily derived from the many definite compounds which it forms with the acids, it appears to be 28 times that of hydrogen. The carbonate, sulphate, nitrate and muriate of soda, are all well known salts. From a comparison of my own experiments with those of others on the proportions of these salts, free from water, I deduce the following

per cent

Carbonate of soda	40 4 acid,	+	59 6 base, as	19	28
Sulphate	—	54 8	—	45 2	—
Nitrate	—	57 6	—	42 4	—
Muriate	—	44	—	56	—
				22	28

These proportions scarcely differ 1 per cent from those of Kirwan and other good authorities. The numbers 19, 34, 38 and 22 being the weights of the respective atoms of acids, the number 28 must be the weight of an atom of soda. Hence we find that soda is a peculiar element, differing from every one we have yet determined in weight. From the weight of the element soda, it may be suspected to be a compound of water, oxygen, or some of the lighter elements, but from present appearances, no such suspicion seems well founded. Soda should then with propriety, be treated

as an elementary principle We shall proceed to the hydrate, the carbonate, and the hydruret of soda, for reasons which have been given under the head of potash .

6 *Hydrate of Soda*

Soda, in what has till lately been considered its pure state, is combined with water The smallest portion of water seems to be one atom to one of soda , that is, 8 parts of water by weight to 28 of soda, or 22 per cent of water I have not obtained soda purer than that of d'Arcet of 72 per cent , but it always contained some carbonic acid and other impurities, which incline me to conclude that 78 per cent would be the highest attainable purity , this may be called the first hydrate it is hard and brittle, and twice the weight of water. The second, third, fourth, and fifth hydrates are, I apprehend, crystalline , but my experience does not warrant me to decide upon their nature , the sixth, and those with more water, are all liquid at the ordinary temperature , their specific gravity is obtained in the usual way, and the corresponding quantity of real alkali is ascertained by the test acids

The following Table for soda, is constructed after the manner of that for potash (page 476).

It will be found moderately accurate, but I could not give it the attention it deserves. Nothing of the kind has been published to my knowledge, yet, such tables appear to me so necessary to the practice of chemical enquiries, that I have wondered how the science could be so long cultivated without them.

That solution which will be found most convenient for a test, is of the specific gravity 1 16 or 1 17, and contains 14 per cent by measure of real alkali, consequently, 100 measures require the same volume of acid tests for their saturation.

Table of the quantity of real soda in watery solutions of different specific gravities, &c

Atoms. Soda Water	Soda per cent by weight	Soda per cent by measure	Specific gravity	Congealing point	Boiling point
1 + 0	100	230 ³	2 30?	unknown	unknown
1 + 1	77 8	156	2 00	1000°	red hot
1 + 2	63 6	118	1 85	500°	600°
1 + 3	53 8	93	1 72	250°	400°
1 + 4	46 0	76	1 63	150°	300°
1 + 5	41 2	64	1 56	80°	280°
1 + 6	36 8	55	1 50		265°
	34	50	1 47		255°
	31	45	1 44		248°
	29	40	1 40		242°
	26	35	1 36		235°
	23	30	1 32		229°
	19	25	1 29		224°
	16	20	1 23		220°
	13	15	1 18		217°
	9	10	1 12		214°
	4 7	5	1 06		213°

7 *Carbonate of Soda*

The salt I call *carbonate of soda*, is to be had of the druggists in great purity, under the name of purified sub-carbonate of soda. It is obtained in the form of large crystals, containing much water, but when exposed to the air for some time, these crystals lose most of their water, and become like flour. I took 100 grains of fresh crystallized carbonate of soda, and exposed it to the action of the air in a saucer. In 1 day it was reduced to 80 grains, in 2 days, to 64 grains, in 4 days, to 49 grains, in 6 days, to 45 grains, in 8 days, to 44 grains, and in 9 days it was still 44 grains, had the appearance of fine dry flour, and probably would have lost no more weight. It was then exposed to a red heat, after which it weighed 37 grains nearly. Now, it is a well established fact, that the common carbonate of soda, heated red, is constituted of 19 parts of acid and 28 of soda, or 40 4 acid and 59 6 base, per cent nearly. Klaproth says, 42 acid, 58 base, Kirwan says, 40 1 acid, 59 9 base. It is equally well established that the crystallized carbonate recently formed in a low temperature, contains about 63 per cent water, as above determined. All experience confirms

this, Bergman and Kirwan find 64 parts of water, Klaproth 62, and d'Arcet 63 6 Hence the constitution of the crystallized carbonate is easily ascertained, for, if 37 63 47 ($= 19 + 28$) 80, the weight of water attached to each atom of the carbonate, that is, 10 atoms of water unite to 1 of carbonate of soda to form the common crystals Again, if 47 8 37 63 = the weight of water attached to 37 parts of carbonate of soda, to correspond with 1 atom of water, but $37 + 63 = 43\frac{3}{4}$, from this it appears that 100 parts of crystallized carbonate being reduced to 44 or $43\frac{3}{4}$, indicates that all the 10 atoms of water are evaporated, except one It should seem, then, that the ordinary efflorescence of this salt is not dry carbonate, but 1 atom of carbonate and 1 of water This supposition is confirmed by experience, for, in 5 days the above 37 grains of heated carbonate became 44 grains by exposure to the air

There is another very remarkable character of the carbonate of soda, which, however, I apprehend will be found to arise from a general law in chemistry, when a quantity of common crystallized carbonate is exposed to heat in a glass retort, as soon as it attains a temperature about 150° , it becomes fluid as water, but when this fluid is heated to 212° ,

and kept boiling a while, a hard, small grained, salt is precipitated from the liquid, which, upon examination, I find to be the *fifth* hydrate, or one atom of carbonate of soda united to 5 atoms of water For, 100 grains of this salt lose 46 by a red heat , but 1 atom of carbonate weighs 47, and 5 atoms of water weigh 40, together making 87 , now, if 87 of such salt contain 40 water, 100 will contain 46 — The clear liquid resting upon the fifth hydrate has the specific gravity 1 35 , on cooling, the whole liquid crystallizes into a fragile, icy mass, which dissolves with a very moderate heat This appears by the test acid to be constituted of 1 atom of carbonate and 15 atoms of water. Thus the tenth hydrate, by heat, is resolved and converted into the fifth and fifteenth , in like manner, probably, the fifteenth might be transformed into the tenth and thirtieth hydrate When any solution below 1 35 sp gravity is set aside to crystallize, the fifteenth hydrate is formed in the liquid, and finally the residuary liquid is reduced to the sp gravity of 1 18 By treating this liquid solution with the test acids, it will be found to consist of 1 atom of carbonate to 30 of water It is of course that solution which the common crystals of carbonate always form, when duly agitated with water or a *saturated* solution at

the mean ordinary temperature of the atmosphere By heat, other liquid solutions may be obtained from 1 85 to 1 35 , but they soon crystallize , such may be called *supersaturated* solutions

The different species of hydrates in crystals have different specific gravities, as might be expected , that of the fifteenth is 1 35 , that of the tenth is 1 42, and that of the fifth 1 64 These were found by dropping the crystals into solutions of carbonate of potash till they were suspended, or by weighing them in saturated solutions of the same I could not ascertain that of the pure carbonate and the first hydrate

When carbonate of soda is used for a test alkali, the specific gravity 1 22 would be that solution which contains 14 per cent by measure of alkali, of which 100 measures would require 100 of test acid for saturation , but, as that solution cannot be preserved without partial crystallization, it will be better to substitute a solution of half the strength , namely, that of 1 11 , then 200 measures of the solution will require 100 of test acid

The following Table contains the characters of various combinations of carbonate of soda and water, resulting from my investigations

Table of the quantity of real carbonate of soda in watery compounds of different specific gravities

Atoms Carb Soda. Water	Carb Soda per cent by weight	Carb Soda per cent by measure	Specific gravity	Congealing point	Boiling point.
1 + 0	100	200?	2 00?	unknown	unknown.
1 + 1	85 5	162?	1 90?	—	—
1 + 5	54	89	1 64	—	—
1 + 10	37	52 5	1 42	150°	
1 + 15	28 8	39	1 35	80°	220°
1 + 20	22 7	28	1 26		217°
1 + 30	16 4	19 5	1 18		214°
		15	1 15		—
		10	1 10		213°
		5	1 05		—

The state of the carbonates in the above table it may be proper to notice The pure carbonate is in the state of a dry powder, so is the first hydrate, not to be distinguished in appearance from the pure carbonate The fifth hydrate may be obtained in a crystalline mass, by heating the common carbonate till a proper portion of water is driven off Its specific gravity is then easily found The tenth hydrate is the common carbonate of the shops in crystals The fifteenth hydrate may be had either in a liquid or solid form, as has been observed The twentieth hydrate is a liquid without any remarkable distinction that I have discovered It is liable to partial crystallization The thirtieth hydrate is a liquid, being the saturated solution at common tem-

perature, this would probably wholly crystallize at no very reduced temperature. The 2d, 3d, 4th, 6th, &c hydrates, I have not found to offer any remarkable discrimination.

8 *Sodium, or Hydruret of Soda*

According to the present state of our knowledge, the account of sodium given at page 262, will require some modification. As the article from which sodium has always been obtained is the first hydrate of soda, and as in the electrization of fused hydrate of soda, no gas is given out, according to Mr Davy, but oxygen, it follows of course that sodium must be a compound of soda and hydrogen, which may be called a hydruret of soda. Mr Davy, conceiving soda in a state of fusion to be pure or free from water, as was the common opinion at the time, concluded that in the electrization of it the soda was decomposed into sodium and oxygen. This conclusion does not now appear to be tenable, though Mr Davy still adheres to it, without having shewn what becomes of the water acknowledged to be present in every instance of the formation of sodium and potassium (Philos Trans 1809), to

the amount of 16 per cent upon the compound

Though Mr Davy's original method of obtaining sodium by Voltaic electricity is the most instructive, as to the nature of the new product, yet, that of Gay Lussac and Thenard is the most convenient when a quantity of the article is required. That is, to pass the vapour of red hot hydrate of soda over iron turnings in a gun barrel, heated to whiteness. The hydrate seems to be decomposed in two ways, in part it is resolved into sodium, or hydruret of soda, and oxygen, the former of which distils into a cooler receptacle of the barrel, and the latter unites to the iron, in part, the hydrate is decomposed into water and soda, and the former again into oxygen, which unites to the iron, and hydrogen which escapes, whilst the soda unites to the iron or its oxide, forming a white metallic compound.

The specific gravity of sodium is stated by Mr Davy at 9348. The weight of its ultimate particle (being 1 atom of soda and 1 of hydrogen) must be 29, and not 21, as stated at page 263. Consequently, 100 parts of the first hydrate of soda, or fused soda, contain 80.6 sodium and 19.4 oxygen per cent. This agrees with that one of Mr Davy's experiments which gave the least portion of oxygen.

Sodium amalgamates with potassium, according to Gay Lussac and Thenard, in various proportions, and the alloys are more fusible than either of the simple metals, being in some cases liquid at the freezing point of water In general, the properties of sodium are found to agree with those of potassium so nearly, as not to require distinct specification.

SECTION 12

EARTHS

The class of bodies called *earths* by chemists are nine in number, their names are *Lime*, *Magnesia*, *Barytes*, *Strontites*, *Alumine* or *Argil*, *Siler*, *Yttria*, *Glucine* and *Zircone* The three last are recently discovered and scarce

The earths constitute the bases of the fossil kingdom Though they have frequently been suspected to be compound bodies, and several attempts have been made to decompose them, it does not yet appear but that they are simple or elementary substances Some of the earths possess alkaline properties, others are without such properties, but they all partake of the following characters 1 They are incombust-

tible, or do not unite with oxygen , 2 they are inferior to the metals in lustre and opacity , 3. they are sparingly soluble in water , 4 they are difficultly fusible, or resist great heat without alteration , 5 they combine with acids ; 6 they combine with each other, and with metallic oxides , and, 7 their specific gravities are from 1 to 5

The latest attempt to decompose the earths is that of Mr Davy , he seems to have shewn, that some of the earths are analogous to the fixed alkalies, in respect to their properties of forming metals , but these metals, like those of the alkalies, are most probably compounds of hydrogen and the respective earths.

1 *Lime*

This earth is one of the most abundant , it is found in all parts of the world, but in a state of combination, generally with some acid When united with carbonic acid, it exists in large strata or beds in the form of chalk, limestone, or marble , and it is from some of these that lime is usually obtained

The common method of obtaining lime, is to expose pieces of chalk or limestone in a kiln for a few days to a strong red or white heat , by this process, the carbonic acid is driven off,

and the lime remains in compact masses of nearly the same size and shape as the limestone, but with the loss of $\frac{2}{5}$ ths of its weight It is probable, the intermixture of the limestone and coal in the combustion of the latter contributes, along with the heat, to the decomposition The lime from chalk is nearly pure, but that from common limestone contains from 10 to 20 per cent of foreign substances, particularly alumine, silex, and oxide of iron

Lime thus obtained, which is commonly called *quicklime*, is white and moderately hard, but brittle Its specific gravity, according to Kirwan, is 2.8 It is corrosive to animal and vegetable substances, and, like the alkalies, converts coloured vegetable infusions, particularly blue, into green It is infusible It has a strong attraction for water, so as to rob the atmosphere of its vapour, when exposed to the atmosphere, it gradually imbibes water, and in a few days falls down into a fine white dry powder, in this process, if pure, it acquires 33 per cent in weight, after this, it begins to exchange its water for carbonic acid, and carbonate of lime is slowly regenerated When 1 part of water is thrown upon 2 of quicklime, the lime quickly falls to powder with intense heat, calculated to be 800' (page

89), this operation is called *slaking* the lime, and is preparatory to most of its applications, the new compound is denominated *hydrate of lime*, and appears to be the only proper combination that subsists between lime and water. By a red heat the water is driven off and the lime remains pure.

As lime combines with the principal acids hitherto considered, and forms with them perfectly neutral salts, and as the proportions of these salts have been experimentally ascertained with precision, we are enabled to determine the weights of an atom of lime thus,

	Acid	Base		
Carbonate of lime,	44	+ 56	per cent as 19	24
Sulphate	—	58 6 + 41 4	—	34 24
Nitrate	—	61 9 + 38 7	—	38 24
Muriate	—	47 8 + 52 2	—	22 24

Carbonate of lime is, I believe, universally allowed to contain either 44 or 45 per cent of acid, and sulphate is mostly supposed to contain 58 per cent acid, the extremes being 56 and 60. The proportions of the other two salts have not been so carefully determined, but it is easy to satisfy one's self that the proportions assigned are not wide of the truth. Let 13 grains of chalk be put into 200 grain measures of the test nitric acid (1 143), or the

test muriatic (1 077), and it will be found that the lime will be wholly dissolved, and the acids saturated Hence it follows that the elementary atom of lime weighs 24 I have formerly stated it at 23, supposing carbonate of lime to be, according to Kirwan, 45 acid + 55 lime per cent The difference is scarcely worth consideration , but experience seems to warrant 24 rather than 23 for the atom of lime

When a large quantity of water is thrown upon a piece of quicklime, it sometimes refuses to slake for a time , perhaps this is caused by the water preventing the rise of temperature In this case the water does not dissolve the lime , hence it should seem that lime properly speaking is not soluble in water , but hydrate of lime is readily soluble, though in a small degree The solution is called *lime-water*, and is a very useful chemical agent

Lime-water may be formed by agitating a quantity of hydrate of lime in water , distilled or rain water should be preferred One brisk agitation is nearly sufficient to saturate the water , but if complete saturation is required, the agitation should be repeated two or three times After the lime has subsided the clear liquid must be decanted and bottled for use Authors differ as to the quantity of lime dis-

solved by water some say that water takes $\frac{1}{500}$ of its weight of lime, others, $\frac{1}{50}$. The fact is, that few have tried the experiment with due care Dr Thomson, in the 4th ed of his chemistry says, from his experience, $\frac{1}{50}$. This is much nearer the truth than the other two One author says, that water of 212° takes up double the quantity of lime that water of 60° does, but deposits the excess on cooling no experimental proof is given If he had said *half* instead of double, the assertion would have been nearly true I have made some experiments on this subject, and the results are worth notice

When water of 60° is duly agitated with hydrate of lime, it clears very slowly, but a quantity of the lime-water may soon be passed through a filter of blotting paper, when it becomes clear and fit for use I found 7000 grains of this water require 75 grains of test sulphuric acid for its saturation Consequently it contained 9 grains of lime. If a quantity of this saturated water, mixed with hydrate of lime, be warmed to 130° and then agitated, it soon becomes clear, 7000 grains of this water decanted, require only 60 grains of test sulphuric acid in order to produce saturation The same saturated lime-water was boiled with hydrate of lime for two or three minutes, and

set aside to cool without agitation, it very soon cleared, and 7000 grains being decanted, required only 46 grains of test acid to be neutralized, the test acid being as usual 1 134. Hence we deduce the following table

1 part water of	takes up of lime	takes up of dry hydrate of lime
60°	7 $\frac{1}{8}$	5 $\frac{1}{4}$
130°	9 $\frac{1}{2}$	7 $\frac{1}{2}$
212°	1 $\frac{1}{2}$	9 $\frac{1}{2}$

This table leads us to conclude that water at the freezing temperature would take nearly twice the quantity of lime that water at the boiling temperature takes, I had not an opportunity to try this in the season of these experiments, but I am informed the calico-printers find a sensible difference in lime-water in different seasons of the year, and that in winter it is most subservient to their purpose, and least so in summer As water takes up so small a portion of lime, and cold water more than warm, one would suppose it was the effect of *suspension* rather than *solution* With this view I tried whether the addition of a little gum to the water would not increase its solvent power, but the result was, that water of 60° took precisely the same quantity of lime, whether with or without gum I found that a deep earthen vessel which had stood some

months with lime-water exposed to the air, still contained $\frac{1}{5}$ of its weight of lime

Lime-water has an acrid taste, notwithstanding the small quantity of lime. It operates on colours like the alkalies. Certain blue colours, such as syrup of violets, are changed to green, infusion of litmus, which has been converted from blue to red by a little acid, has its blue colour restored by lime-water, and archil solution, reddened by an acid, is restored to its purple colour by lime-water. When exposed to the air, lime-water has a thin crust formed on its surface, this is carbonate of lime, the acid being derived from the atmosphere, it is insoluble, and falls to the bottom, in time the whole of the lime is thus converted into carbonate, and the water remains pure. If a person breathes through a tube into lime-water, it is rendered milky through the formation of carbonate, or if water containing carbonic acid be poured into it, but a double quantity of the acid forms a supercarbonate of lime, which is soluble in a considerable degree. Though lime is soluble in water in so small a quantity, yet a portion of distilled water may be mixed with $\frac{1}{5}$ of its bulk of lime-water, and the presence of lime will be shewn by the test colours, or by nitrate of mercury, &c.

Lime combines with sulphur and with phos-

phorus these compounds will be considered under the heads of sulphurets and phosphurets It combines also with the acids, and forms with them neutral salts Lime unites to certain metallic oxides, particularly those of mercury and lead, but the nature of these last compounds is not much known

One of the great uses of lime is in the formation of mortar In order to form mortar, the lime is slaked and mixed up with a quantity of sand, and the whole well wrought up into the consistence of paste with as little water as possible This cement, properly interposed amongst the bricks or stones of buildings, gradually hardens and adheres to them so as to bind the whole together This is partly, perhaps principally, owing to the regeneration of the carbonate of lime from the carbonic acid of the atmosphere The best ingredients and their proportions to form mortar for different purposes, do not seem yet to be well understood

2 *Magnesia*

This earth is obtained from a salt now called *sulphate of magnesia*, which abounds in sea-water and in some natural springs According to the best analyses, crystallized sulphate of

magnesia consists of 56 parts of pure dry sulphate, and 44 parts water in the hundred. Some authors find more water in this salt; namely, from 48 to 53 per cent, but Dr. Henry, in his analysis of British and foreign salt, in the Philos Trans 1810, takes notice of a crystallized sulphate of magnesia containing only 44 per cent water, and the specimen of sulphate which I have had for many years bears the same character I am, therefore, inclined to adopt this as the true proportion of water Now, Dr Henry found that 100 grains of the above sulphate of magnesia produced 111 or 112 grains of sulphate of barytes, and it is well established that $\frac{1}{3}$ of this last salt is acid, hence, the sulphuric acid in 100 sulphate of magnesia (56 real) is equal to 37 grains, consequently the magnesia is equal to 19 grains but the weight of an atom of sulphuric acid is 34, therefore, 37 : 19 :: 34 : 17, nearly, which must be the weight of an atom of magnesia, on the supposition that sulphate of magnesia is constituted of one atom of acid united to one of base, of which there is no reason to doubt I have in the first part of this work, page 219, stated the weight of magnesia to be 20, it was deduced chiefly from Kirwan's analysis of sulphate of magnesia, but

from present experience I think it is too high
Though few of the salts of magnesia have been
analyzed with great precision, yet the weight
of the atom of magnesia derived from different
analyses would not fall below 17, nor rise
above 20 Dr Henry and I analyzed the
common carbonate of magnesia well dried in
100°, and found it to lose 40 per cent by acids,
and 57 per cent by a moderate red heat Hence
it should consist of 43 magnesia, 40 carbonic
acid, and 17 water We found the carbonate
begin to give out water and some acid about
450°, but it supported a heat of 550° for an
hour without losing more than 16 per cent
Hence the carbonate must be constituted of 1
atom of acid, 1 of magnesia, and 1 of water,
stating the magnesia at 20 , for, $19 + 8 + 20 = 47$, and if 47 19, 8, and 20 100 40,
17 and 43 respectively, according to the above
experiments I have reason to think, however,
that the weight of the atom of magnesia ought
rather to be deduced from the sulphate than
the carbonate , because it is probable that this
last always contains a small portion of sulphate
of lime, when prepared by the medium of
common spring water, this portion will be
found in the result of the analysis by fire, and
will be placed to the account of magnesia

Wherefore I conclude the weight of an atom of magnesia to be 17 It is said that a super-carbonate of magnesia is obtainable , but when sulphate of magnesia and supercarbonate of soda in solution are mixed together, there is a great effervescence and disengagement of carbonic acid, and nothing but the common carbonate of magnesia is precipitated according to my experience Dr Henry, indeed, obtained a crystallization by exposing a dilute mixture for some time , the crystals were small opake globules, about the size of small shot , but upon examination, they proved to be nothing but carbonate of magnesia united to 3 atoms of water instead of 1 atom For, 100 grains lost 70 by a red heat, and 30 by acids , whence its constitution was 30 acid + 30 earth + 40 water, or 19 acid + 19 earth + 24 or 25 water The constitution of crystallized sulphate of magnesia must, therefore, be 1 atom of acid + 1 atom of magnesia + 5 atoms of water , in weight $34 + 17 + 40 = 91$, this gives per cent 37 acid + 19 base + 44 water, agreeably to Dr Henry's experience above-mentioned

The constitution of the most common salts of magnesia, in their dry state will, therefore be as under

	Acid	Base				
Carbonate of magnesia	53	+ 47	per cent. as 19	17		
Sulphate	—	— 66 7	+ 33 3	—	— 34	17
Nitrate	—	— 69	+ 31	—	— 38	17
Muriate	—	— 56 4	+ 43 6	—	— 22	17

The nitrate of magnesia in the above table agrees with that of Kirwan, and Richter, and the muriate with that of Wenzel

To obtain magnesia, the sulphate must be dissolved in water, and a quantity of pure potash in solution must be added , the magnesia is then thrown down, and may be separated by filtration Or if carbonate of potash be put into the solution of sulphate of magnesia, carbonate of magnesia will then be precipitated, which may be separated by filtration , this last must be exposed to a red heat to drive off the carbonic acid , the former need only to be dried in a gentle heat

Magnesia is a white, soft powder, possessing little taste and no smell , its specific gravity is said to be 2 3 It operates on vegetable colours like lime and the alkalies It is infusible by heat, and very sparingly soluble in water According to Kirwan, it requires 7000 times its weight of water to dissolve it , I found it require 16,000 times its weight of water in one experiment When exposed to the air,

magnesia, like lime, attracts 1 atom of water to 1 of magnesia, amounting to about 47 per cent by my experience; it attracts carbonic acid but very slowly. It does not combine with any of the simple substances, except perhaps hydrogen and sulphur. With the acids it forms neutral salts, which are found frequently to combine with other salts.

As the sulphate of magnesia is the ordinary combination of this earth exhibited as a soluble salt, it may be of use to have a table shewing the quantity of real dry sulphate, and of ordinary crystallized sulphate, in given weights or measures of solutions of different specific gravities. The table is founded on my own experience.

Table of sulphate of magnesia

Atoms. Mag Water	Dry sulphate of magnesia per cent by weight	Dry sulphate of magnesia per cent by measure	Common crystal- lized sulphate of mag per cent by measure	Specific gravity
1 + 0	100			
1 + 5	56	93	166	1 66 sol
1 + 8	44 4	66 6	119	1 50 liq
1 + 10	39	55 4	99	1 42
1 + 15	30	39	69 6	1 30
		31	55	1 25
		24	42 8	1 20
		18	32 1	1 15
		12	21 4	1 10
		6	10 7	1 05

The fifth hydrate is the ordinary crystallized sulphate, the eighth is the strongest liquid so-

lution obtained by boiling , and the fifteenth is a saturated solution at 60°

3 *Barytes*

The earth now denominated *barytes*, was discovered by Scheele in 1774 Since then the labour and experience of several distinguished chemists have added much to the knowledge both of the earth and its compounds , so that now it may perhaps be said to be the best understood of all the earths It occurs most frequently in combination with sulphuric acid, the compound being called *sulphate of barytes*, formerly *ponderous spar*, and is found about mines, particularly of copper It also occurs in combination with carbonic acid, though rarely , the compound is denominated *carbonate of barytes*

Barytes may be obtained either from the sulphate or the carbonate The former must be pulverized, mixed with charcoal, and exposed in a crucible to a red heat for some hours , the sulphate is thus changed into a sulphuret This sulphuret is to be treated with nitric acid, when the sulphur is thrown down, and the barytes combines with the acid , the acid may then be driven off by a red heat and barytes will remain in the crucible If the carbonate

be used, it must be pulverized, mixed with charcoal, and exposed for some time in a crucible to the heat of a smith's forge Boiling water will then dissolve the pure barytes, leaving the charcoal and carbonate, and upon cooling, crystals of hydrate of barytes are obtained The greatest part of the water may be driven off by heat

Pure barytes obtained by the former method is a greyish white body, easily reduced to powder It has a harsh and caustic taste, and if swallowed proves poisonous Like lime, when exposed to the atmosphere, it absorbs water, and then parts with it for carbonic acid It changes certain vegetable blues to green Its specific gravity is nearly 4 Barytes forms various combinations with water, called *hydrates*, which will presently be mentioned It combines with sulphur and phosphorus, but not with the other simple substance The sulphuret and phosphuret will be considered under their respective heads The weight of the ultimate particle of barytes can be very nearly approximated, and appears to be 68, or twice the weight of an atom of sulphuric acid This appears from the following statement of the proportions of the most common barytic salts, which have been successfully investigated

	Acid.	Base.			
Carbonate of barytes	22	+ 78	percent as 19	68	
Sulphate	— — —	33 3 + 66 7	— — —	34	68
Nitrate	— — —	36 + 64	— — —	38	68
Muriate	— — —	24 4 + 75 6	— — —	22	68

The following respectable authorities agree in assigning 22 per cent acid to carbonate of barytes, namely, Pelletier, Clement, Desormes, Klaproth, and Kirwan, and more recently Mr. Aikin finds 21 67, and Mr James Thomson, 21 75 (Nicholson's Journal, vol 22 and 23, 1809) The last mentioned chemist finds sulphate of barytes to be 33 acid, and 67 barytes. His conclusion corroborates the previous ones of Withering, Black, Klaproth, Kirwan, Bucholz, and Berthier, who all fix the acid at or near 33 per cent Vauquelin, Rose, Berthollet and Thenard and Clement and Desormes find 32 or more acid, and Fourcroy and Aikin, 34 It is very satisfactory to see the near coincidence in regard to the constitution of this salt, because it is frequently made a test of the quantity of sulphuric acid and of sulphur Mr J Thomson finds 59 3 barytes per cent in nitrate of barytes, Clement and Desormes 60, Kirwan 58 and 55 at different trials, and Fourcroy and Vauquelin 50 These results differ considerably from each other, and are all below the proportion as-

signed above, but it must be observed that crystallized nitrate of barytes contains water, and perhaps various quantities of water according to the temperature in which it crystallizes, now, if the atom of nitrate be associated with 1 atom of water, then the proportion of barytes per cent will be 59 6, which nearly agrees with Thomson, and Clement and Desormes, if with 2 atoms of water, the barytes will be 55 7 per cent, if with 3 atoms, then 52 3, &c — Crystallized muriate of barytes appears clearly to consist of an atom of dry muriate + 2 atoms of water, or 22 acid + 68 barytes + 16 water, this reduced gives 20 8 acid + 64 1 barytes + 15 1 water per cent — For, Kirwan finds 20 acid + 64 base + 16 water, Fourcroy, 24 acid + 60 base + 16 water, and Aikin, 22 9 acid + 62 5 base + 14 6 water per cent, which agree with each other, and with the theory as nearly as can be expected

Barytes combines with most acids, and forms with them neutral salts In many respects it appears to be related to the fixed alkalies, only in weight it is nearly the same as both of them put together

Hydrate of Barytes

When pure barytes, obtained from the nitrate by heat, is exposed to the air, or is moistened by water, it combines with it, and that in various degrees, forming a number of *hydrates*, which have not been sufficiently attended to and discriminated, much heat is evolved during the combination it was mistaking the first hydrate of barytes for pure barytes that caused the uncertainty for some time in regard to the proportions of the elements of sulphate of barytes (see page 474) Now, if an atom of barytes weigh 68, the first hydrate will weigh 76, to which if 34 sulphuric acid be added, we shall have an atom of sulphate of barytes = 102, (for the water is driven off by the union of the acid and base), if then we conceived the hydrate to be pure barytes we should conclude that 76 barytes united to 26 sulphuric acid to form 102 sulphate, which is very near the former mistaken conclusion of Thenard and Berthollet Hence then there is reason to conclude that their barytes, kept some time in a red heat, was in reality the first hydrate, or one atom of barytes and one of water When pure barytes is dissolved in boiling water, a solution is formed of specific gravity

exceeding 12, on cooling, great part of it crystallizes, these crystals are the *twentieth* hydrate, or consist of 1 atom of barytes and 20 of water, or 30 barytes and 70 water per cent; if they are exposed to a heat about 400° or 500° , they melt, great part of the water is dissipated, and a dry white powder is obtained, which is the *fifth* hydrate. In this operation, 228 parts ($= 68 + 20 \times 8$) are reduced to 108 ($= 68 + 5 \times 8$), or 100 to 47, which is exactly the reduction obtained experimentally by Dr Hope. This dry powder melts below a red heat, but I have not been able to find what it would be reduced to by exposure to a red heat, because it acquires carbonic acid, even in a crucible, as Berthollet has observed, almost as fast as it loses water. My experience on the crystals of barytes has been limited, but from the following I conclude they are the *twentieth* hydrate. I took 80 grains of fresh crystallized barytes, and dissolved them in 1000 grains of water, the solution was of the specific gravity 1 024, this solution took 70 grain measures of test sulphuric acid to saturate it, and afforded 36 grains of dried sulphate of barytes of this 12 grains were acid and 24 barytes. Whence we learn, 1st, that 80 grains of crystals are equal to 24 real barytes, or 228 equal to 68, but $228 = 20 \times 8 + 68$, which shews that 20 atoms of

water are united to 1 of barytes, 2d, that the decimals in the second and third places of the expression for the specific gravity, denote the quantity of real barytes in 1000 grain measures of the solution. This last must evidently hold without any material error in all the inferior solutions, and hence the strength and value of barytic water may be known by its specific gravity, an advantage which does not practically appertain to lime water. By subsequent trials, however, I found the quantity of barytes rather overrated.

The following sketch of a table of the hydrate of barytes may have its use, till a more ample and correct one can be constructed.

Table of the Hydrate of Barytes

Atoms Baryt Water	Barytes per cent by weight	Barytes per cent by measure	Specific gravity	Congealing point.
1 + 0	100	400?	4 00 ³ sol	unknown
1 + 1	90	—	—	—
1 + 5	63	—	—	—
1 + 20	30	48	1 6	—
1 + 30	19	25	1 3	fl
1 + 275	2 6	2 7	1 03	—*
	1 8	1 9	1 02	—
	0 9	0 9	1 01	—

4 Strontites

The mineral from which this earth is obtained was first found in the lead-mine of Strontian in Argyleshire, Scotland. The earth and

* This is a saturated solution in the mean temperature of 60°.

its distinguishing properties, were pointed out by Dr Hope in an essay read to the Royal Society of Edinburgh, in 1792, and published in their Transactions, 1794. Several distinguished chemists have since confirmed and extended these investigations. The Scotch mineral is a *carbonate* of strontites, but the earth has since been found in various parts combined with sulphuric acid.

Strontites is obtained from the sulphate or carbonate of strontites, by the same processes as barytes from the like compounds, indeed, it bears so close a resemblance to barytes, both in its free and combined state, as to have been confounded with it. Strontites has much the same acrid taste as barytes, but it is not poisonous, it is less soluble in water than barytes, it has the property of giving a red or purple colour to flame, for which purpose the nitrate or muriate may be dissolved in alcohol, or applied to the wick of a candle. The weight of the atom of strontites is deducible from the salts which it forms with the more common acids to be 46. Thus,

	Acid	Base		
Carbonate of strontites	29.2	+ 70.8 per cent	as 19	46
Sulphate	—	42.0	+ 57.5	34 46
Nitrate	—	45.2	+ 54.8	38 46
Muriate	—	32.4	+ 67.6	22 46

Dr Hope, Pelletier, and Klaproth find 30 per cent of acid in the carbonate Klaproth, Clayfield, Henry, and Kirwan find 42 per cent. acid in the sulphate Kirwan finds the crystallized nitrate to contain 31.07 acid, 36.21 base, and 32.72 water, which I presume denotes 1 atom of acid, 1 of base, and 5 of water, that is, 38 acid + 46 base + 40 water, this reduced, would give 30.6 acid, 37.1 base, and 32.3 water per cent which very nearly agrees with his experience Taking the dry salt, his results would give 46.2 acid, and 53.8 base Vauquelin finds the nitrate to contain 48.4 acid, 47.6 base, and 4 water, but this constitution cannot be correct Neither can Richter's analysis, which gives 51.4 acid and water, and 48.6 base — Dry muriate of strontites, according to Kirwan, consists of 31 acid, and 69 base, but Vauquelin states 39 acid, and 61 base, the former, without doubt, is nearer the truth

Hydrate of Strontites When water is put to pure strontites, it becomes hot and swells, like lime and barytes, and falls into dry powder This powder seems to be the first hydrate, whence, 46 parts of strontites will take 8 of water to form this combination, but if more water be added, the hydrate crystallizes These crystals appear to be the 12th hydrate,

that is, they are constituted of 1 atom of strontites and 12 of water = $46 + 96 = 142$, or 32 strontites + 68 water per cent agreeably to the experience of Dr Hope. Water dissolves about $\frac{1}{16}$ th of its weight of pure strontites in the temperature of 60° , or $\frac{1}{5}$ th of its weight of the crystals, the specific gravity of the solution is nearly 1 008 But boiling water dissolves about half its weight of the crystals. Whence it appears that strontites is much less soluble than barytes, and much more soluble than lime. The specific gravity of the crystals of strontites is rightly determined by Hassenfratz to be nearly 1 46 Strontian water may be used for the same purposes as lime-water, or barytic water

Strontites combines with most of the acids to form neutral salts It also combines with sulphur and phosphorus

5 Alumine, or Argil

The earth denominated alumine, constitutes a great portion of common *clay*, but this last is a mixture of two or more earths with iron, &c, and therefore cannot be exhibited as pure alumine The earth may be obtained pure from a common well known salt, called *alum*,

which is constituted of sulphate of potash and sulphate of alumine combined together, with a portion of water A quantity of alum is to be dissolved in 10 times its weight of water, to this a quantity of liquid ammonia is to be added, the sulphuric acid seizes the ammonia, and lets fall the alumine, which may be separated from the liquid by filtration, and then exposed to a red heat

Alumine thus obtained is a fine white earth, spongy, and adhesive when moistened, it has neither taste nor smell, it is said to have the specific gravity, 2 When mixed with water, it forms a mass which is the basis of earthen ware, and capable of receiving any figure In this case, by the application of great heat, it becomes excessively hard, and loses in part, or wholly, its adhesive quality Pure alumine bears the highest heat of a furnace without undergoing any change

Alumine does not form any known combination with oxygen, hydrogen, charcoal, sulphur, or phosphorus, but it combines with the alkalies, with most of the earths, and with several metallic oxides It combines too with many of the acids, but forms in most cases uncrystallizable salts It possesses a strong affinity for vegetable colouring matter, and hence its great importance in the arts of dyeing and

printing, in which it is employed to fix the colour on the cloth

The weight of an atom of alumine is not so easily determined as that of the preceding earths and alkalies, partly because the salts which it forms with the acids are not crystallizable, and partly because they have not had a proportionate share of attention paid to them. The only salt with alumine which has been carefully analyzed is the triple compound, or alum, an acquaintance with the constitution and properties of this salt is of great importance to its manufacturer, and to the various artists to whom it is of indispensable utility

The experience of Chaptal, Vauquelin, and of Thenard and Roard (*Ann de Chimie*, vol 22, 50, and 59, or *Nicholson's Journal*, vol 18) shews that the alum of all countries is very nearly the same in its constitution and qualities, that it contains 33 per cent sulphuric acid, 11 or 12 alumine, 8 or 9 potash, and 47 water All the authors I have mentioned do not agree, it is true, in these numbers, but the differences are more in appearance than reality Vauquelin obtains 95 sulphate of barytes from 100 alum, but Thenard and Roard obtain 100 The last mentioned chemists adopt only 26 per cent acid in sulphate of barytes, whereas it is now universally allowed there are about

33 per cent. acid in that salt. Mr James Thomson, I am informed, finds nearly 100 per cent sulphate of barytes. This result I adopt as the most correct, and it is also the most recent Vauquelin finds $48\frac{1}{2}$ water in alum, this is more than is generally found, and accounts in some degree for his obtaining less sulphate of barytes Chaptal finds 47 per cent. water in English alum, with which my experience accords Vauquelin finds 10 5 alumine, Thenard and Roard, 12 5 per cent. Mr Tennant of Glasgow, who favoured me with an analysis, finds 11 2 alumine in the alum manufactured there This last chemist finds 15 per cent sulphate of potash, which is the same as Thenard and Roard's nearly, 15 7 Now, as 34 acid + 42 potash, have been shewn to constitute 76 sulphate, 15 must contain 6 7 acid and 8 3 potash Collecting these results then, it appears that alum may be said to consist of,

33 sulphuric acid

11 7 alumine

8 3 potash

47 water

Of the 33 sulphuric acid, it must be recollect that 6 7 parts belong to the potash, that is, $\frac{1}{3}$ th of the whole, the remainder, or $\frac{4}{3}$ ths, belong to the alumine Hence, then, were there only 5 atoms of sulphuric acid in a molecule of alum, 1 atom would appertain to an atom of potash, and the other 4 atoms to as many of alumine, provided the acid and alumine unite one to one, which we are to presume till sufficient reason appear to the contrary It should seem, then, that an atom of alum is constituted of one of sulphate of potash in the centre, and 4 atoms of sulphate of alumine around it, forming a square But $33 - 6 7 = 26$ 3 acid to 11 7 alumine, and $26 \times 3 + 11 \times 7 = 34 + 15$, the weight of an atom of alumine Dry alum must, therefore, be $5 \times 34 + 42 + 4 \times 15 = 272$, but as this is found combined with water in the state of common alum, it will be satisfactory to know how many atoms of water are attached to one atom of dry alum for this purpose, we have $272 - 211 =$ the weight of water, this, divided by 5, gives the number of atoms = 30 Hence, an atom of common alum consists of,

1 atom of sulphate of potash = 76 = percent 15

1 atoms of sulphate of alumine = 196 ————— 38

And 30 atoms of water = 240 ————— 47

————— 12 ————— 100

A saturated solution of alum in water, at the temperature 60° , is of the specific gravity 1 048, and is constituted of 1 atom of dry alum and 600 of water, or the alum has 20 times the quantity of water that the crystals contain. The specific gravity of alum itself is about 1 71, and by means of heat, solutions of it in water may be obtained of any inferior specific gravity, at least, I have had a solution, which, when hot, was 1 57.

Alumine does not combine with carbonic acid, but it combines with the nitric and muriatic acids, it would, therefore, be desirable that the weight of an atom of alumine should be investigated from these last combinations, as well as from the sulphate. No author that I know has given the proportion of elements in nitrate of alumine, and in muriate of alumine. Bucholz determines equal parts of acid and base, and Wenzel 28 acid to 72 base, so that no confidence can be placed in them. I determined the proportions of these salts as follows. 100 grains of alum were dissolved in water, the alumine was precipitated by 156 measures, more or less, of test ammonia, (97), care being taken that the aluminous solution was saturated with ammonia, and that none was superabundant, the liquid was then well agitated, and immediately divided into three

equal portions. It was then found that each of these portions took 52 measures of the test acids., namely, the sulphuric, the nitric, and the muriatic respectively, to dissolve the floating alumine, and to clear the solutions which were afterwards found to be free from uncombined acids Hence, the proportions of the salts are deduced as under

	Acid.	Base		
Sulphate of alumine	69 4 + 30 6 per cent.	as 34	15	
Nitrate — — —	71 7 + 28 3 — — —	38	15	
Muriate — — —	59 5 + 40 5 — — —	22	15	

It will be proper here to notice an opinion which Vauquelin supported in his essay in 1797, but which is not adverted to in his succeeding essay in 1804, nor in the one of Thenard and Roard in 1806 I mean the opinion that alum consists of the *supersulphate* of alumine and sulphate of potash If this be true, then the atom of alumine must weigh 30, because 2 atoms of sulphuric acid unite to 1 of alumine The opinion appears to me without support When a solution of alum is put to the blue test, it changes it to red , but this is not a proof of excess of acid where the base of the salt has a strong affinity for colouring matter , there is probably a true decomposition of the salt, or perhaps the colouring matter forms

a triple compound with the salt. That no uncombined acid accompanies alum is certain, because the least portion of alkali decomposes it. Besides, a red heat drives off half of the acid at least from supersalts, but alum bears a red heat without losing a sensible portion of acid. From the experiment related above, it appears that the sulphuric, the nitric, and the muriatic acid tests are of equal efficacy in saturating alumine. Are these all supersalts? If so, why does not half the acid in each case neutralize the earth, and form a simple salt?— But it is said if alumine be boiled in a solution of alum, the alumine combines with the alum, and falls down an insoluble, neutral salt. Vauquelin asserts he has made the experiment, but he mentions no proportions, nor does he point out the time requisite to produce the effect. With a view to this subject, I precipitated the alumine from a measure of saturated solution of alum at 60° (about 100 grains of alum) by the necessary quantity of ammonia, to this liquid, which was found neutral, still containing the alumine in suspension, I put another measure of the same solution of alum, and boiled the whole for 10 minutes in a glass vessel, it was then set aside to cool, and filtered, the liquid was not much diminished in specific gravity, and required nearly the same

quantity of ammonia to saturate it, and afforded the same quantity of alumine as the first measure. Apprehending the sulphate of ammonia present might influence the result, I next put the dry pulverized alumine from 100 grains of alum into a solution of 100 grains of alum in water, and in another experiment the moist recently filtered alumine, and boiled the whole for 10 minutes, the water evaporated was restored, and the liquor filtered, it was of the same specific gravity as at first, tasted equally aluminous, and the precipitate collected and dried, weighed just the same as before These facts lead me to doubt concerning the existence of this *alum saturated with its earth*, as the earlier chemists called it But supposing the existence of a combination of sulphuric acid with twice the quantity of alumine, I know no reason why it should not be constituted of 1 atom of acid and 2 of alumine Hence, I conclude the weight of an atom of alumine above stated is a fair deduction

The French chemists seem to have proved that the presence of even a very small portion of sulphate of iron in alum is very injurious in some of its uses in dyeing, &c

Hydrate of Alumine Saussure, in the 52d vol of the Journal de Physique, observes, that alumine is precipitated from its solution, in

two very different states, according to circumstances, the one he calls *spongy*, and the other *gelatinous alumine*, they both retain 58 parts per cent. of water, when dried in common summer heat, the former parts with the whole of its water at a red heat, but the latter only loses 48 per cent at the highest temperature. There may be some doubt as to the accuracy of these facts, but it would seem probable that alumine, at the ordinary temperature, retains 2 atoms of water, or 15 parts alumine hold 16 of water, this would allow 52 per cent loss by a red heat. The subject deserves further attention.

6 *Silex*

The earth denominated *silex*, is found abundantly in a great many stones, it is almost pure in *flint*, *rock crystal*, and others, but of stones in general it only constitutes a part, being found in combination with one or more of the other earths, or with metals, &c It is also found in small particles in the form of white sand The most distinguishing feature of this earth is its melting along with either of the fixed alkalies, and forming with them that beautiful and well known compound, glass. The specific gravity of flint and rock crystal is usually about 2 65 After being heated red

hot for some time, flint may be pulverized in an iron mortar, and forms a white earth, which may be regarded as silex sufficiently pure for most purposes It forms a harsh, gritty powder, which does not cohere nor form a paste with water like clay It is insoluble in water in any sensible degree It is infusible by heat, unless at an extremely high degree To obtain silex in a pure state, a mixture of sulphuric acid and fluate of lime must be distilled in glass vessels, or along with pulverized flint, when superfluate of silex is produced in an elastic state , the gas may be received over water, on the surface of which a crust of fluate of silex is formed , this crust being removed by filtration or otherwise, the clear liquor is to be saturated with ammonia, when pure silex is thrown down When dried in a red heat, it forms a fine white powder The common mode prescribed to obtain pure silex gives pure glass, as will presently be explained It is remarkable, that sulphuric acid, poured on fluate of silex, expels the fluoric acid in fumes, though it does not combine with the silex

Silex combines with the two fixed alkalies, with most of the earths, and with metallic oxides , but with few of the acids immediately, except the fluoric , when joined to an alkali, it may be united to several of the acids,

forming triple salts It seems not to combine with oxygen, hydrogen, or the other combustibles, nor with ammonia

The fixed alkalies may each be combined with silex in two proportions. In order to form glass, one part of silex and one of fine dry carbonate of soda may be mixed together, but if potash is used, then $1\frac{1}{2}$ parts will be required. If the other or soluble compound is wanted, then double the quantities of alkali must be used, or 2 parts of soda and 3 of potash. A strong red heat in each case is necessary to form a complete union of the principles, the fused mass gives out the carbonic acid of the alkalies, and when poured out immediately becomes glass, but when the double quantity of alkali is used, the glass is deliquescent, and may be completely dissolved in water. This last may be called *supersodiuretted* or *superpotasiuretted silex*, and the former *sodiuretted* or *potasiuretted silex*. When an acid is dropped into a solution of superpotasiuretted silex, a white precipitate is immediately formed, which is potasiuretted silex, or common glass, and not silex, as has hitherto been supposed. For, 1 The heated precipitate, I find, weighs about $\frac{2}{3}$ ds of the red hot potasiuretted silex, whereas the silex is only about $\frac{1}{3}$ d of the compound, 2 the acid requisite to throw down the precip-

pitate, is only half of that which the alkali in the compound would require for its saturation; 3 the precipitate, dried in a moderate red heat, is fusible into glass by the blow-pipe, and, 4 as the acids do not take the alkali from glass, they ought not to take more alkali from superpotasiuretted silex than what would reduce it to common glass

It is more difficult to find the weight of an atom of silex than that of any other of the previous earths, because it enters into combination with only one of the acids, and the proportions have not yet been ascertained I have, however, succeeded pretty well by investigating its relations with potash, lime, and barytes Having obtained a quantity of superpotasiuretted silex without any excess of alkali, that is, which afforded a precipitate with the least portion of acid (for if the alkali be in excess, acid may be added without any precipitation), I precipitated a given weight of the dried compound previously in water, by sulphuric acid in excess, the precipitate was heavy and bulky, after remaining on the filter for some time, it resembled a mass of over boiled potatoe, the water being forced out by pressure, a white substance remained, which easily left the filter, and when dried in a low red heat, left a harsh gritty powder, nearly $\frac{2}{3}$ ds of the weight of the

compound Again, test sulphuric acid was slowly added to the solution, of a given weight of the dry compound in water, as soon as the mixture manifested acid to the test liquid, it was considered as saturated The whole acid added was found to be sufficient to saturate a weight of pure alkali nearly equal to $\frac{1}{3}$ d of that of the dry compound These experiments rendered it obvious that only one half of the alkali was engaged by the acid, the other half remaining with the silex, and the conversion of the precipitate into glass by the blow-pipe confirmed the conclusion It remained, then, to determine which of the two combinations of alkali and silex was the most simple As a part of the alkali is easily drawn from one compound, and difficultly from the other, the former must be supposed two atoms of alkali to one of silex, and the latter one to one From this it should seem, that the weight of an atom of silex is nearly the same as that of an atom of potash, and the near agreement of the specific gravities of these two bodies, is an argument in favour of the conclusion

Superpotasiuretted silex exhibited remarkable results with lime and barytes One hundred measures of the solution, containing 18 grains dry, were saturated with 5000 grains of lime water, containing 6 grains of lime, the

precipitate, filtered and dried in a low red heat, was 19 grains The residuary liquid required 27 grains of test muriatic acid to saturate it , whereas, the like quantity of lime water took 54 grains Here, then, it appears that each atom of the superpotasiuretted silex must have been decomposed into one atom of potash, which remained in the liquid, and one atom of potasiuretted silex, which united to two atoms of lime, and the compound was precipitated That the matter in the liquid was potash, and not lime, was proved by carbonic acid , and the test muriatic acid shewed that every atom of potash in the liquid took the place of two atoms of lime The case was different with barytes One hundred measures of the solution, containing 18 grains dry, were saturated with 850 measures of 10115 barytic water, containing 9 dry barytes The residuary liquid took 28 test acid to saturate it, and the precipitate dried in a red heat was 20 grains Here it is evident that one atom of barytes had detached one of potash from the compound, and taken its place , consequently, the residue of liquid required the same quantity of acid as the barytic water, and the precipitate was a triple compound of silex, potash, and barytes , one atom of each, consisting

probably of 9 parts of barytes, $5\frac{1}{2}$ silex, and $5\frac{1}{2}$ potash

Upon the whole, I am inclined to believe that one atom of silex weighs nearly 45 times that of hydrogen

Silex combines with alumine by heat, and the compound forms hard infusible bodies, such as porcelain, earthen ware, bricks, &c.

7 *Yttria*

This earth is found at Ytterby, in Sweden. It constitutes a portion of the mineral called *gadolinite*, first analyzed by Gadolin, and of that called *yttriotantalite*, both found in the same mine. The earth may be obtained by dissolving the pulverized mineral in a mixture of nitric and muriatic acids, the liquor poured off is then evaporated to dryness, the residuum dissolved in water. If ammonia be now added, the earth is precipitated. It is obtained in the form of a white powder, said to be of the specific gravity 4.81. It is infusible by heat, and insoluble in water but it forms salts with several of the acids, and these salts have mostly a sweet taste, and are in some instances coloured. They resemble the metallic salts in many particulars. According to Klaproth, the

hydrate of yttria, a dry powder, contains 31 per cent water, this would imply that the atom of yttria weighs 18, 36, or 53, according as it is the first, second, or third hydrate, but he finds the carbonate of yttria to be 18 acid, 55 yttria, and 27 water now, supposing the carbonate to be 1 atom of acid, 1 of earth, and 3 of water, and that the acid and water weigh 45, then the atom of earth is deduced to be 53, and this conclusion agrees with the preceding one, which supposes the hydrate to be the third. The great specific gravity of the earth countenances the notion of the atom being heavy, but we cannot rely upon the above determination till it is supported by more various experiments.

8 *Glucine*

The earth called *glucine* (from the sweet-tasted salts which it forms with acids) is obtained chiefly from two minerals, the beryl and the emerald. These minerals are constituted of silex, alumine, and glucine, the two former being abstracted by the usual processes, there remains the glucine, a soft white powder, adhering to the tongue, but without taste or smell, and infusible by heat. Its specific gravity is said to be 2.97. It is insoluble in wa-

ter This earth combines with the acids, with liquid fixed alkalies, and with liquid carbonate of ammonia In the last case it resembles yttria, but is much more soluble than that earth in carbonate of ammonia Glucine has considerable resemblance in its properties both to alumine and yttria.

We have not data sufficient to find the weight of an atom of glucine, but from the experiments of Vauquelin on the carbonate of glucine (Annal de Chimie, tom 26, pages 160 and 172) it should seem to weigh nearly 30, or twice the weight of alumine It is remarkable, too, that the analysis of the beryl, and of the emerald, give nearly the same quantity of alumine and glucine, which indicates that the weight of an atom of the latter is either equal to that of the former, or some multiple of it

9 Zircon

The zircon or jargon, and the hyacinth, are two precious stones found chiefly in Ceylon These contain a peculiar earth which has received the name of zircon It may be obtained thus Let one part of zircon in powder, be fused with 6 parts of potash, then let the mass be diffused through a portion of water,

which will dissolve the potash and its combinations, and leave a residuum This residuum must be dissolved in muriatic acid, and potash must be added, which will precipitate the zircon. It is a fine white powder, insipid, and somewhat harsh to the feel When violently heated, it is converted into a kind of porcelain, very hard, and of the specific gravity 4.35 Zircon is not soluble in water, but it retains $\frac{1}{3}$ or $\frac{1}{4}$ of its weight of water when dried in the air, and assumes the appearance of gum arabic. Zircon is not soluble in liquid alkalies, but it is in the alkaline carbonates, it adheres to several of the metallic oxides Zircon unites with acids, and forms with them salts, many of which are insoluble in water, but others are very soluble They have an astringent taste, resembling some of the metallic salts

As the salts of zircon have not yet been formed with sufficient care to ascertain the ratio of their constituent principles, we can not exactly determine the weight of an atom of this earth Vauquelin finds 44 carbonic acid and water and 56 zircon in carbonate of zircon, but, unfortunately, he has not given the acid separately from the water Allowing the accuracy of the above, and supposing the carbonate to contain 1 atom of water, the weight of an atom of zircon will be 34, but if we

suppose 2 atoms of water, then the atom of earth comes out 45 This last I judge to be nearest the truth It is remarkable, that the hyacinth contains 32 parts of silex and 64 of zircon, which, according to the above conclusion, corresponds to 1 atom of silex and 2 of zircon, a constitution by no means improbable. Upon this principle, the gummy hydrate above mentioned, may be 2 atoms of water and 1 of zircon, or 16 water + 45 zircon.

END OF PART SECOND

EXPLANATION OF PLATES

PLATE 5 Exhibits the various symbols devised to represent the simple and compound elements, they are nearly the same as in plate 4, only extended and corrected they will be found to agree with the results obtained in the preceding pages

Fig	Simple	Wt	Fig	Wt	
1	Oxygen	7	12	Iron	50
2	Hydrogen	1	13	Nickel	25 ? 50 ?
3	Azote	5	14	Tin	50
4	Carbone	5 4	15	Lead	95
5	Sulphur	13	16	Zinc	56
6	Phosphorus	9	17	Bismuth	68 ?
7	Gold	140 ?	18	Antimony	40
8	Platina	100 ?	19	Arsenic	42 ?
9	Silver	100	20	Cobalt	55 ?
10	Mercury	167	21	Manganese	40 ?
11	Copper	56	22	Uranium	60 ?

Fig.		Wt.	Fig.		Wt.
23	Tungsten	56 ?	41	Nitrous gas	12
24	Titanium	40 ?	42,	Nitrous oxide	17
25	Cerium	45 ?	43	Nitric acid	19
26	Potash	42	44	Oxynitric acid	26
27.	Soda	28	45	Nitrous acid	31
28	Lime	24	46	Carbonic oxide	12.4
29	Magnesia	17	47	Carbonic acid	19 4
30	Barytes	63	48	Sulphurous oxide	20
31	Strontites	46	49	Sulphurous acid	27
32	Alumine	15	50	Sulphuric acid	34
33	Silex	45	51	Phosphorous acid	32
34	Yttria	53	52	Phosphoric acid	23
35	Glucine	30	53	Ammonia	6
36	Zircone	45	54	Olefiant gas	6 4
	Compound.		55	Carburetted hyd	7 4
37.	Water	8	56	Sulphuret hydr.	14
38	Fluoric acid	15	57	Supersulph hydr	27
39	Muriatic acid	22	58	Phosphuret. hydr.	10
40	Oxymuriatic acid	29	59	Phosphur sulph.	22
			60	Superphos. sulph	31

PLATE 6 Symbols of compound elements (continued from Plate 5)

Fig.		Wt.	Fig.		Wt.
1	Hydrate of potash	50	16	Muriate of barytes	90
2	Potassium, or hydruret of potash	43	17	Sulphite of alumine	49
3	Carbonate of potash	61	18	Nitrate of alumine	53
4	Hydrate of soda	36	19	Muriate of alumine	37
5	Sodium, or hydruret of soda	29	20	Alum	272
6	Carbonate of soda	47	21	Potasiuretted silex, or glass	87
7	Hydrate of lime	32	22	Superpotasiuretted silex	129
8	Carbonate of lime	43	23	Potash, silex, & lime	135
9	Sulphate of lime	58	24	Potash, silex, & barytes	155
10	Nitrate of lime	62	25	Fluate of silex	60
11	Muriate of lime	46	26	Subpotasiuretted ammonia	54
12	Hydrate of barytes	76	27	Oxymuriate of olephant gas	41
13	Carbonate of barytes	87			
14	Sulphate of barytes	102			
15	Nitrate of barytes	106			

* The olive coloured substance obtained by heating potassium in ammonical gas, by Gay Lussac and Thenard, Davy, &c.

PLATE 7 Fig. 1, 2, and 3 represent profile views of the disposition and arrangement of particles constituting elastic fluids, both simple and compound, but not mixed; it would be difficult to convey an adequate idea of the last case, agreeably to the principles maintained, page 190 — The principle may, however, be elucidated by the succeeding figures.

Fig 4 is the representation of 4 particles of azote with their elastic atmospheres, marked by rays emanating from the solid central atom; these rays being exactly alike in all the 4 particles, can meet each other, and maintain an equilibrium.

Fig. 5 represents 2 atoms of hydrogen drawn in due proportion to those of azote, and coming in contact with them; it is obvious that the atoms of hydrogen can apply one to the other with facility, but can not apply to those of azote, by reason of the rays not meeting each other in like circumstances, hence, the cause of the intestine motion which takes place on the mixture of elastic fluids, till the exterior particles come to press on something solid

PLATE 8 The first 16 figures represent the atoms of different elastic fluids, drawn in the centres of squares of different magnitude, so as to be proportionate to the diameters of the atoms as they have been herein determined Fig 1 is the largest, and they gradually decrease to fig 16, which is the smallest, namely, as under,

Fig	Fig
1 Superfluate of silex	9 Oxymuriatic acid
2 Muriatic acid	10 Nitrous gas
3 Carbonic oxide	11 Sulphurous acid
4 Carbonic acid	12 Nitrous oxide
5 Sulphuretted hydrogen	13 Ammonia
6 Phosphuretted hydrogen	14 Olefiant gas
7 Hydrogen	15 Oxygen
8 Carburetted hydrogen	16 Azote

Fig 17 exhibits curve lines, by which the boiling point of liquid solutions of nitric and muriatic acid, and of ammonia, of any strength, may be determined They are representations of the results contained in the preceding tables relative to these articles If any point be taken in one of the curves, and a horizontal line be traced to the margin, the strength per cent by weight of the liquid will be shewn, and if a perpendicular line be traced to the top the temperature at which the liquid of that strength boils in the open air will be found

APPENDIX.



AS it is nearly two years since the printing of this second part commenced, it may be expected that in the rapid progress of chemical investigation, some addition has, in the interval, been made to the stock of facts and observations relating to the more early subjects herein discussed. The ground upon which I determine the weights of the ultimate particles of the metals, has not yet been entered upon. This will occupy a leading place in a second volume, when the metallic oxides and sulphurets come to be considered. It will be observed, that I have seen reason to change some of the metallic weights which were given in the first part, and it is probable, that in our future investigations these may be again changed, this will depend upon the precision with which the proportions of the elements of the metallic oxides, sulphurets and salts, shall be obtained. The identity of tantalum and columbium seems to have been ascertained by

Dr Wollaston Mr Davy, and the French chemists Gay Lussac and Thenard, have furnished a number of facts and observations on various subjects, resulting from their application of the new metals, potassium and sodium, and Voltaic electricity, to chemical investigations When the mind is ardently engaged in prosecuting experimental enquiries, of a new and extraordinary kind, it is not to be expected that new theoretic views can be examined in all their relations, and formed so as to be consistent with all the well known and established facts of chemistry , nor that the facts themselves can be ascertained with that precision which long experience, an acquaintance with the instruments, and the defects to which they are liable, and a comparison of like observations made by different persons, are calculated to produce This may appear to be a sufficient apology for the differences observed in the results of the above celebrated chemists, and for the opposition, and sometimes extravagance, of their views

All the phenomena of combustion are exhibited by heating potassium in fluoric acid gas (superfluate of silex) , though this would seem to intimate that the gas contains oxygen, yet, as Mr Davy properly observes, heat and light

are merely the results of the intense agency of combination It is remarkable that hydrogen is given out, yet not so much as would be given by the action of potassium on water , it is variable, and amounts generally to less than $\frac{1}{4}$ th of that quantity Mr Davy and the French chemists agree in the belief of a decomposition of the acid , but it is doubtful whether the hydrogen is from the potassium or the acid The fact, I have observed, page 285, of the diminution of a mixture of hydrogen and fluoric acid gas by electricity, is one of the strongest in favour of the notion that the acid gas contains oxygen

Muriatic acid has been a great object of investigation Mr Davy's ideas on this subject, in his Electrochemical Researches, 1808, were, that the acid gas contains water in a combined state , or, to use my own phraseology, that an atom of real muriatic acid combined with one of water, formed one of the acid gas , hence, in burning potassium in the gas, the potassium decomposed the water, the hydrogen was liberated, and the oxygen joined to the potassium to form potash, with which the real or dry acid immediately united This conclusion was plausible , but it was truly astonishing to see the French chemists draw the same conclusion

from their views of the subject They should have viewed muriatic acid gas as the pure acid, which combined with the potash of the potassium, and liberated its hydrogen Mr Davy has recently written an essay on the oxymuriatic and muriatic acids, with a copy of which he has just favoured me , in this, he discards his former opinion of the gaseous combination of acid and water, and adopts another, that muriatic acid gas is a pure elastic fluid, resulting from the union of hydrogen with oxymuriatic acid, which last he conceives to be a simple substance This notion agrees so far with mine, as to make hydrogen the base of muriatic acid , but I cannot adopt his constitution of the acid Mr Davy now considers the hydrogen liberated, by the combustion of potassium in muriatic acid gas, as proceeding from the decomposed acid, and the new compound an *oxymuriate of potassium* The explanation I prefer is, that the hydrogen proceeds from the potassium, and the undecomposed acid gas unites to the potash

As to oxymuriatic acid, Gay Lussac and Thenard have reported some very striking and unexpected properties of it which they have discovered They assert, that dry oxymuriatic acid gas was not decomposed by sulphurous

acid gas, nitrous oxide, carbonic oxide, nor even nitrous gas, when these were dry, but that it was immediately decomposed by them if water was present These *may* appear to them to be facts, but certainly they are too important, and some of them too difficultly ascertained, to be believed merely upon the assertion of any one By what means were they found? What was the structure of the apparatus, the quantity of gases operated upon, the time they were allowed to be in contact, the means employed to investigate the results, &c &c? To answer all these enquiries satisfactorily, would require a volume in detail, yet, Gay Lussac and Thenard have not said one word Now, we know that the facts respecting the mixtures of these gases over water, are *not* as above stated Mr Davy observes, (Researches, page 250) that " oxygenated muriatic acid and nitrous oxide " were mingled in a water apparatus, there " was a slight appearance of condensation, " but this was most probably owing to absorption by the water, on agitation, the oxygenated muriatic acid was absorbed, and the " greater part of the nitrous oxide remained un- " altered " I have repeatedly mixed carbonic oxide and nitrous gas with oxymuriatic acid in a water apparatus, the former mixture ex-

hibits no signs of chemical union for several seconds, afterwards, if the sun shine upon it, chemical action commences, and continues somewhat slower than that of oxygen and nitrous gas; but if the mixture be put in the dark, it will remain for days, I believe, without any change. The latter mixture, or nitrous gas and oxymuriatic acid, in equal measures, over water, produces an instantaneous union, much more rapid than that of oxygen and nitrous gas, and which to all appearance seems independent upon the water. Now, if these simple experiments give such different results in different hands, what may we expect of the complex experiments, where the gases are previously dried, and then mixed in vessels quite free from mercury and water, and lastly examined after such mixture has taken place, regard being still had to the effects which mercury and water have, or are supposed to have, upon such mixtures?

Mr Davy has given several experiments to shew that oxymuriatic acid combines with hydrogen to produce muriatic acid, but none of them appears to me decisive. When equal measures of hydrogen and oxymuriatic acid were introduced into an exhausted vessel, and fired by an electric spark, the result was a

slight vapour, and a condensation of $\frac{1}{10}$ to $\frac{1}{20}$ of the volume, the gas remaining being muriatic acid This fact, if it can be relied upon, is favourable to the notion it is to support , I should have expected a condensation of $\frac{1}{3}$ or $\frac{1}{4}$ of the total volume on the common hypothesis , if the author had described the apparatus and quantity of gases submitted to the experiment, with the mode of determining the quantity and quality of the residual gas, it would have assisted in any future enquiry on the subject , it is certainly an important experiment Mr. Davy allows the hyperoxymuriate of potash to abound with oxygen He supposes the oxygen to be attracted by the potassium, or the potash, rather than by the oxymuriatic acid The facts appear to me to draw the other way much more powerfully We find oxymuriatic acid in conjunction with much oxygen, in several other salts, but potash no where, except when joined to this acid

Some observations on nitric acid, and the other compounds of azote and oxygen, have been made by Gay Lussac, in the 2d vol of the Memoires d'Arcueil He contends that one *measure* of oxygenous gas unites to two *measures* of nitrous gas to form nitric acid, and to three measures to form nitrous acid Now

I have shewn, page 328, that 1 measure of oxygen may be combined with 1 3 of nitrous gas, or with 3 5, or with any intermediate quantity whatever, according to circumstances, which he seems to allow, what, then, is the nature of the combinations below 2, and above 3, of nitrous gas? No answer is given to this, but the opinion is founded upon an hypothesis that all elastic fluids combine in equal measures, or in measures that have some simple relation one to another, as 1 to 2, 1 to 3, 2 to 3, &c In fact, his notion of measures is analogous to mine of atoms, and if it could be proved that all elastic fluids have the same number of atoms in the same volume, or numbers that are as 1, 2, 3, &c the two hypotheses would be the same, except that mine is universal, and h's applies only to elastic fluids Gay Lussac could not but see (page 188, Part 1 of this work) that a similar hypothesis had been entertained by me, and abandoned as untenable, however, as he has revived the notion, I shall make a few observations upon it, though I do not doubt but he will soon see its inadequacy

Nitrous gas is, according to Gay Lussac, constituted of equal measures of azote and oxygen, which, when combined, occupy the same volume as when free He quotes Davy, who

found 44.05 azote, and 55.95 oxygen by weight, in nitrous gas He converts these into volumes, and finds them after the rate of 100 azote to 108.9 oxygen There is, however, a mistake in this, if properly reduced, it gives 100 azote to 112 oxygen, taking the specific gravities according to Biot and Arago But that Davy has overrated the oxygen 12 per cent he shews by burning potassium in nitrous gas, when 100 measures afforded just 50 of azote The degree of purity of the nitrous gas, and the particulars of the experiment, are not mentioned This one result is to stand against the mean of three experiments of Davy, (see page 318) and may or may not be more correct, as hereafter shall appear Dr Henry's analysis of ammonia embraces that of nitrous gas also , he finds 100 measures of ammonia require 120 of nitrous gas for their saturation Now this will apply to Gay Lussac's theory in a very direct manner , for, according to him, ammonia is formed of 1 measure of azote and 3 of hydrogen, condensed into a volume of 2 , it follows, then, that 100 ammonia require 75 oxygen to saturate the hydrogen , hence, 120 nitrous gas should contain 75 oxygen, or 100 should contain 62.5, instead of 50 Here either the theory of Gay Lussac, or the expe-

rience of Dr Henry, must give results wide of the truth In regard to ammonia too, it may farther be added, that neither is the rate of azote to hydrogen 1 to 3, nor is the volume of ammonia doubled by decomposition, according to the experiments of Berthollet, Davy, and Henry, made with the most scrupulous attention to accuracy, to which may be added my own —There is another point of view in which this theory of Gay Lussac is unfortunate, in regard to ammonia and nitrous gas , 1 measure of azote with 3 of hydrogen, forms 2 of ammonia , and 1 measure of azote with 1 of oxygen, forms 2 of nitrous gas now, according to a well established principle in chemistry, 1 measure of oxygen ought to combine with 3 of hydrogen, or with one half as much, or twice as much , but no one of these combinations takes place If Gay Lussac adopt my conclusions, namely, that 100 measures of azote require about 250 hydrogen to form ammonia (page 433), and that 100 azote require about 120 oxygen to form nitrous gas (page 331), he will perceive that the hydrogen of the former would unite to the oxygen of the latter, and form water, leaving no excess of either, further than the unavoidable errors of experiments might produce , and thus the great

chemical law would be preserved The truth is, I believe, that gases do not unite in equal or exact measures in any one instance , when they appear to do so, it is owing to the inaccuracy of our experiments In no case, perhaps, is there a nearer approach to mathematical exactness, than in that of 1 measure of oxygen to 2 of hydrogen , but here, the most exact experiments I have ever made, gave 1 97 hydrogen to 1 oxygen

I shall close this subject, by presenting two tables of the elements of elastic fluids , they are collected principally from the results already given in detail, with a few small alterations or corrections , the utility of them to practical chemistry will be readily recognised.

Tables of the elements of elastic fluids; at a mean temperature and pressure

(TABLE I.)

Names of the gases	Wt. of an atom	Wt. of 100 cubic inch gra.	Specific gravity	Diameter of an atom	No. of atoms in a given volume.
Atmospheric air	—	31	1 00	—	—
Hydrogen	1	2 5	08	1 000	1000
Oxygen	7	34	1 10	794	2000
Azote	5	30 2	97	747	2400
Muriatic acid	22	39 5	1 21	1 12	700
Ammonia	6	18 6	60	909	1330
Oxymur acid	29	76	2 16	981	1060
Nitrous gas	12	32 2	1 04	980	1060
Nitrous oxide	17	50	1 60	947	1180
Carbonic oxide	12 4	29	94	1 020	940
Carbonic acid	19 4	47	1 52	1 00	1000
Sulphurous acid	27	71	2 30	95	1170
Olefiant gas	6 4	29 5	95	81	1890
Carburetted hyd	7 4	18 6	60	1 00	1000
Sulphureted hyd	14	36	1 16	1 00	1000
Phosphur hyd	10	26	84	1 07	1000
Superflu of silex	75	130	4 20	1 15	658

(TABLE 2)

Proportions of the constituent principles of compound gases

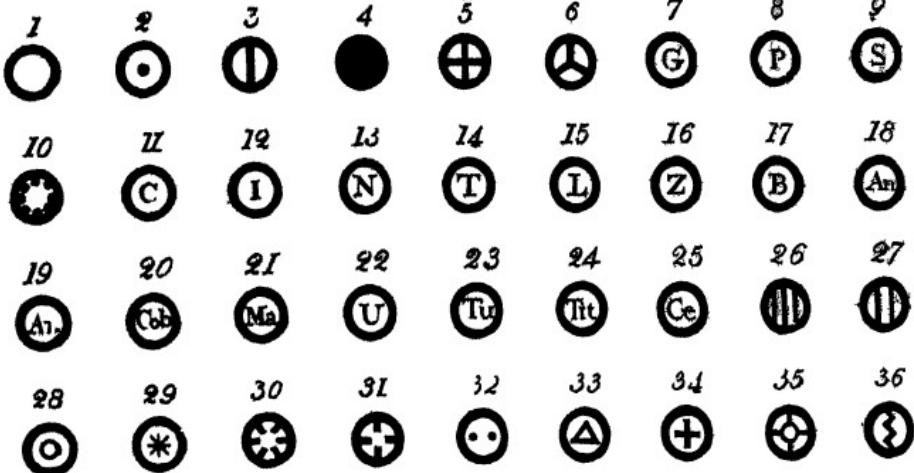
Names of the compound gases	Constituent principles of 100 measures of the compound gases.	Constituent principles of 100 weight of the compound gases.
	Measures	Measures
Ammon gas	52 azote + 133 hyd	83 azote + 17 hyd
Water	100 oxyg + 200 hyd *	97 oxy + 12.5 hyd
Nitrous gas	46 azote + 55 oxyg	47 azote + 58 oxygen
Nitr oxide	99 azote + 58 oxyg	99 azote + 41 oxygen
Nitric acid	180 nit gas + 100 oxy	27 azote + 73 oxy
Nitrous acid	360 nit gas + 100 oxy	33 azote + 67 oxy
Oxym acid	150 mur acid + 50 oxy	76 mur acid + 24 oxy
Sulphs acid	100 oxygen + sulphur	72 oxy + 18 sulphur
Sulphic acid	100 sulphur acid + 50 oxy	79 sul acid + 20½ oxy
Carb oxide	47 oxy + charcoal	55 oxy + 15 charc
Carb acid	100 oxy + charcoal	72 oxy + 28 charc
Carbon hyd	200 hydr + 1 part carb	27 hyd + 73 charc
Olephant gas	200 hyd + 2 parts carb	15 hyd + 55 charc
Sulph hyd	100 hyd + sulphur	7 hyd + 93 sulph
Mur of am	100 mur acid + 100 am g	65 mur acid + 35 am gas
Carb of am	100 carb acid + 80 am g	76 carb acid + 24 am gas
Sube of am	100 carb acid + 160 am g	61 carb acid + 39 am gas

* I believe 197 is nearer the truth.

ELEMENTS

Simple

Plate 5

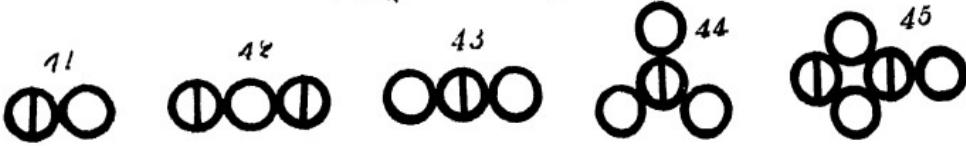


Compound

Oxygen with Hydrogen



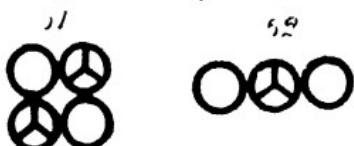
Oxygen with Azote



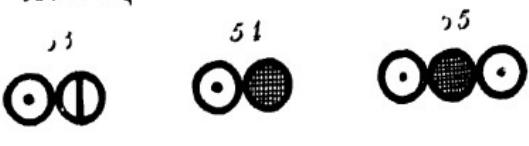
Oxygen with carbon and Sulphur



Oxygen with phosph



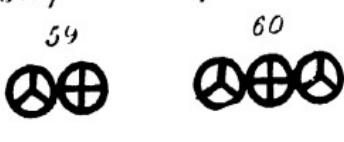
Hydrogen with azote & carbon



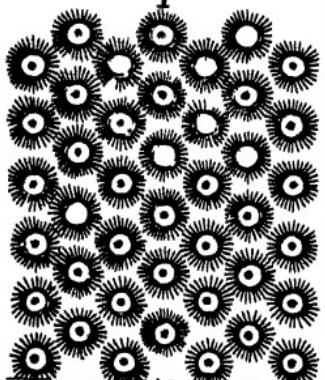
Hyd with sulph & phosph



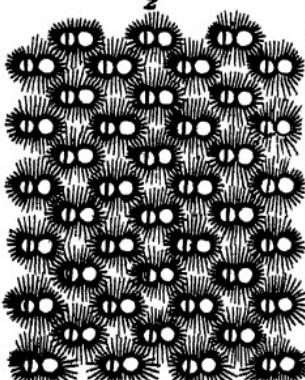
Sulphur with phosph



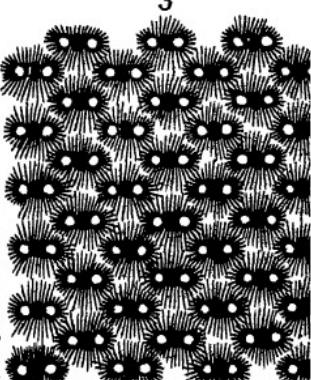
Hydrogen gas



Nitrous gas

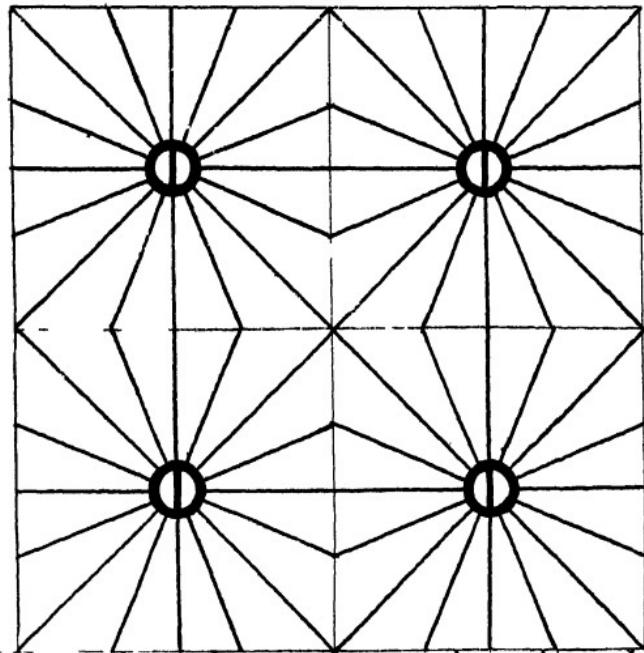


Carbonic acid gas



4

Acet



5

Hydrog

